STUDIES ON REACTIVITY OF 2-MERCAPTO-3-PHENYL-4-QUINAZOLINONE AND N-ETHOXYCARBONYL THIOPHENE-2-HIOCARBOXAMIDE TOWARDS METAL IONS & SUBSTITUTION CTIONS OF $[RuCl_3(AsPh_3)_2(CH_3OH)]$, $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ AND trans-$[Rh(CO)Cl(MPh_3)_2](M=P, As)$ WITH SOME THIOCARBOXA(I)MIDES

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By

HARI KISHAN GUPTA

to the

DEPARTMENT OF CHEMISTRY

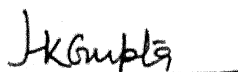**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**

JULY 1986

पूज्यनीया माता जी
एवं
पूज्य पिताजी
को
सादर समर्पित

Dedicated to my
Parents

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Dr. S.K. Dikshit.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

HARI KISHAN GUPTA

Kanpur:
July 1986.

CERTIFICATE

Certified that the work contained in this thesis entitled: Studies on Reactivity of 2-Mercapto-3-phenyl-4-quinazolinone and N-Ethoxycarbonylthiophene-2-thiocarboxamide Towards Metal Ions & Substitution Reactions of $[RuCl_3(AsPh_3)_2(CH_3OH)]$, $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ and trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P, As) With Some Thiocarboxa-(i)mides, has been carried out by Mr. Hari Kishan Gupta, under my supervision and the same has not been submitted elsewhere for a degree.

(S. K. DIKSHIT)
Thesis Supervisor

Kanpur :
July 1986.

DEPARTMENT OF CHEMISTRY,
INDIAN INSTITUTE OF TECHNOLOGY KANPUR, INDIA
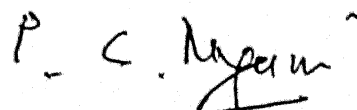

CERTIFICATE OF COURSE WORK

This is to to certify that Mr. Hari Kishan Gupta has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 505   Principles of Organic Chemistry

Chm 524   Modern Physical Methods in Chemistry

Chm 525   Principles of Physical Chemistry

Chm 541   Advanced Inorganic Chemistry I

Chm 542   Advanced Inorganic Chemistry II

Chm 545   Principles of Inorganic Chemistry

Chm 800   General Seminar

Chm 801   Special Seminar

Chm 900   Post-Graduate Research

Mr. Hari Kishan Gupta was admitted to the candidacy of the Ph.D. degree programme in May 1983 after he successfully completed the written and oral qualifying examinations.

(P.S. Goel)
professor and Head,
Department of Chemistry,
IIT-KANPUR

(P. C. Nigam)
Convener,
Departmental Post-
Graduate Committee
Dept. of Chemistry,
IIT-KANPUR

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HARI KISHAN GUPTA

PREFACE

The coordination chemistry of 2-mercapto-3-phenyl-4-quinazolinone and specially thiocarboxamide ($R_1CSNHCOR_2$) ligands is in its infancy and only within the past few years has some understanding of the properties of these ligands been gained. In contrast, the related monothio-β-ketones have been under study for several years. There remains a remarkable interest in monothio-β-ketone ligands, the thiocarboxamides promise to provide an equally rich chemistry. The real impetus towards developing the coordination chemistry of these potential ligands has been provided by the possibility of their ruthenium, palladium and platinum complexes having antitumor and anticancer activity (these compounds reported in Ind. J. Chem., 23A, 204 (1984), are under anticancer screening at National Cancer Institute, USA). Added to this, the recent observations of involvement of sulphur containing molecules in conjunction with a few transition metal ions in various enzymatic and metabolic processes have given a further challange to the chemists. Designing of the sulphur containing model molecules mimicing those involved in natural processes ranks among the prime goals of inorganic chemistry.

The present thesis is only a little attempt in this direction. The work mainly concerns the complexing behaviour of title ligands.

The thesis begins with a chapter on a brief literature survey related to the present understanding of thioamide bands

and their application in deciding bonding site. Substitution reactions of $[RuCl_3(AsPh_3)_2(CH_3OH)]$, $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ and trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P, As) with variety of ligands is also described.

In the second Chapter, the synthetic details and characterisation of 2-mercapto-3-phenyl-4-quinazolinone (MPQH) complexes of Co(II), Ni(II), Pd(II), Pt(II) and Pt(IV) ions with and without various N-heterocyclic bases have been described.

The third Chapter encompasses the reactions of Mn(II), Ru(III) and Rh(III) salts with MPQH in the presence and absence of N-bases. The gross geometrical features of some of the Mn(II) and Ru(III) complexes were ascertained with the help of e.s.r. studies.

Chapter four embodies the studies on reactivity of N-ethoxy-carbonylthiophene-2-thiocarboxamide (ETH) towards transition and non-transition metal ions under different conditions.

Fifth Chapter describes the substitution reactions of $[RuCl_3(AsPh_3)_2(CH_3OH)]$ and $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ with several thiocarboxa(i)mides.

In the last sixth Chapter, the reactivity of thiocarboxa-(i)mides towards trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P, As) has been studied and with the help of analytical, magnetic and spectral data, their structures have been proposed.
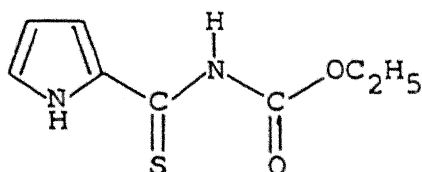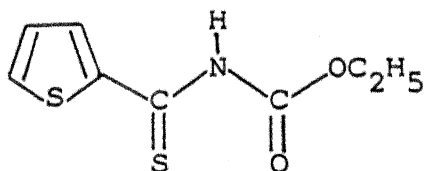
ABBREVIATIONS

i)
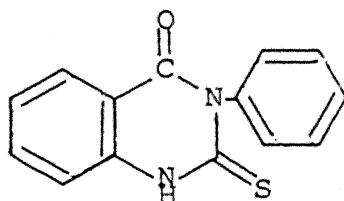
2-Mercapto-3-phenyl-4-quinazolinone (MPQH)
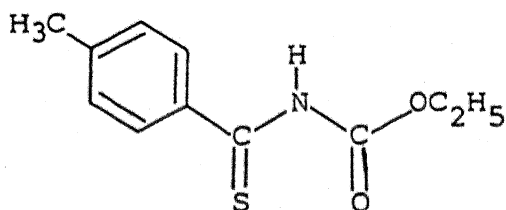
ii)

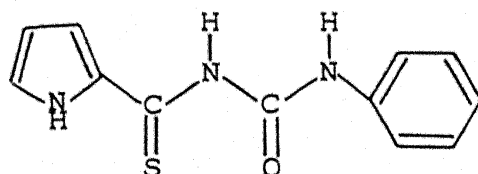N-Ethoxycarbonylpyrrole-2-thiocarboxamide (EPH)

iii)

N-Ethoxycarbonylthiophene-2-thiocarboxamide (ETH)

iv)

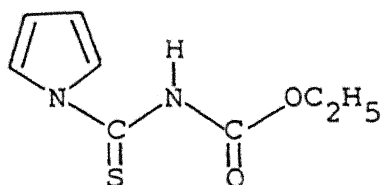N-Ethoxycarbonyltoluene-4-thiocarboxamide (ETOLH)
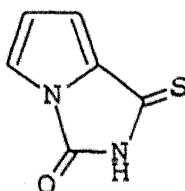
v)

N-Phenylcarbamoylpyrrole-2-thiocarboxamide (PPH)

Abbreviations (contd.)

vi)

N-Ethoxylcarbonylpyrrole-1-thiocarboxamide (EPTH)

vii)

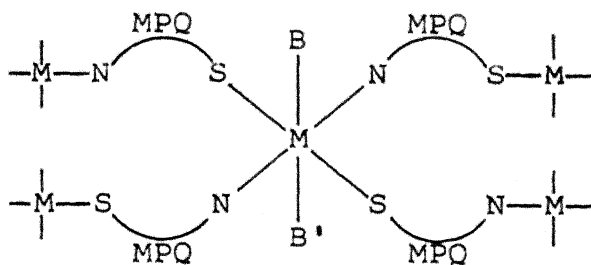2-Thiopyrrole-1,2-dicarboximide (TPH)

SYNOPSIS

Ligating properties of thiocarboxa(i)mides and 2-mercapto-3-phenyl-4-quinazolinone have been recently investigated.[1-4] The purpose of this work has been to both extend and more fully define the chemistry of this important class of ligands. In the present study an attempt has been made to explore the following:

i) Identification of donor sites with the aid of i.r. spectral data;

ii) Relative importance of various resonance and tautomeric forms of the ligands for different metal ions and their contribution to the electronic structure of resulting co-ordination compounds

iii) Changes in both chemical reactivity and structural proper-ties of thiocarboxa(i)mides and their complexes induced by alterations in the peripheral structure of the coordi-nated ligand;

iv) Determination of stereochemistry of the products based on magnetic and n.m.r., e.s.r., electronic spectral data.

MPQH, ETH, ETOLH, EPH, PPH, TPH and EPTH have been chosen to study their complexing behaviour towards Mn(II), Co(II), Ni(II), Ru(II), Ru(III), Rh(I), Rh(III), Pd(II), Pt(II), Pt(IV), Cu(II), Ag(I), Pb(II), Cd(II) and Hg(II) ions. Reactions of title ligands with $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$, $[Rh(CO)(Cl)(MPh_3)_2]$ (M = P, As); $[RuCl_3(AsPh_3)_2CH_3OH]$ and $[Rh(PPh_3)_3Cl]$ have been carried out and the products characterized.

The first introductory chapter of the thesis presents in brief the salient features of the nature of the thioamide group containing and related sulphur ligands.

In the second chapter, the reactions of 2-mercapto-3-phenyl-4-quinazolinone (MPQH) with Co(II), Ni(II), Pd(II), Pt(II) and Pt(IV) ions in the presence of various N-heterocyclic bases such as, pyridine, β-picoline, o-phenanthroline, 2,2'-bipyridine, imidazole, pyrazole and pyrimidine are described. In all these reactions, the alkaline ethanolic solution (pH $\approx$ 9-10) of ligand MPQH has been used. Ni(MPQ)$_2$ in contrast to earlier report[4] has been assigned tetrahedral geometry based on the magnetic moment value of 3.74 B.M. Rest of the complexes formed in the presence of bases are high spin octahedral with the exception of Co(MPQ)$_2$(pzH) which is trigonal bipyramidal (TBP). The i.r. spectra of the complexes indicate that MPQH is coordinated through its exocyclic sulphur and imino-nitrogen atoms simultaneously. All the compounds reported in this chapter are sparingly soluble in most of the common organic solvents. Based on this observation and undue strain involved in four membered chelates, polymeric structures of the complexes have been preferred over monomeric chelates. This is worthwhile to mention that several four membered chelate rings with NS ligands are known[5] where the large size of the sulphur atom is supposed to reduce the undue strain in the ring.

$$
\begin{array}{c}
\text{—M—N} \overset{\text{MPQ}}{\diagdown}\text{S} \qquad \text{B} \qquad \text{N}\overset{\text{MPQ}}{\diagup}\text{S—M—} \\
\text{M} \\
\text{—M—S} \underset{\text{MPQ}}{\diagup}\text{N} \qquad \text{B'} \qquad \text{S}\underset{\text{MPQ}}{\diagdown}\text{N—M—}
\end{array}
$$

The third chapter deals with the reactions of Mn(II), Ru(III) and Rh(III) salts with MPQH in the presence and absence of various N-heterocyclic bases in alkaline medium. $MnCl_2.4H_2O$ reacts with alkaline alcoholic solution of MPQH to yield brown oxo-manganese complex MnO(MPQH). Similarly the reactions of MPQH with Mn(II) salt in the presence of bases lead to the formation of $MnO(MPQH)_2.B$ (B = py, β-pic or o-phen) and $MnO(H_2O)$-$(MPQH)_{1/2}(bipy)$. $RuCl_3.3H_2O$ gives $[Ru(MPQ)_2Cl.DMF]$ in DMF medium and $Ru(MPQ)_2Cl.2H_2O$ in alkaline alcoholic medium. In the presence of heterocyclic bases, complexes $[Ru(MPQ)_2Cl.B]H_2O$ (B = py, β-pic or imzH) and $[Ru(MPQ)Cl_2(o-phen)]H_2O$ are obtained. Ruthenium complexes showed the magnetic moment at room temperature equivalent to one unpaired electron and oxo-manganese complexes, except MnO(MPQH), equivalent to five unpaired electrons. The 4.24 B.M. magnetic moment of MnO(MPQH) is in good agreement with square planar geometry. Both Mn(II) and Ru(III) complexes were subjected to e.s.r. studies and their distortion parameters were calculated. The d-orbitals energies were also calculated for some of Ru(III) complexes.

In Chapter four, studies on the complexing behaviour of ETH towards several transition and non-transition metal ions

have been presented. Aqueous solution of $CuCl_2.2H_2O$ reacts with ETH below 5 $^{\circ}$C to give the square planar complex of formula $Cu(Et)_2$ and if this solution is heated under reflux for about 3 hr, cupric sulphide is obtained. Aqueous solution of $Ni(NO_3)_2.6H_2O$ reacts with ETH in the presence of excess pyridine at 5 $^{\circ}$C to yield $Ni(ET)_2(py)$. The deprotonated form of the ligand (ET) is coordinated through N and S simultaneously in both Cu(II) and Ni(II) complexes. An aqueous $AgNO_3$ solution gives immediate yellow precipitate with ETH at room temperature which was characterised as AgET. This reaction under reflux condition yields Ag_2S and oxygenated form of ligand (N-ethoxycarboxylthiophene-2-carboxamide). The reactions of ETH with other salts of soft metal ions such as Pb(II), Cd(II) and Hg(II) under reflux conditions yield the corresponding sulphides. The $Pd(ET)_2$ and $Pt(ET)_2$ were obtained from the reaction of ETH with $PdCl_2.2H_2O$ and $PtCl_4.5H_2O$, respectively. The refluxing of $MCl_3.3H_2O$ (M = Ru, Rh) with ETH in aqueous/ethanol medium resulted in the formation of octahedral complexes of the type $[M(ET)_2Cl.H_2O]$. The infrared spectra suggest the simultaneous involvement of N and S of deprotonated ligand in Pd(II), Pt(II), Ru(III) and Rh(III) complexes while in AgET, ET is coordinated through N and O atoms. When the compound $[RhCl(PPh_3)_3]$ was allowed to react with ETH in CH_2Cl_2/EtOH, it resulted in formation of a dimeric Rh(I) complex, $[Rh(ETH)(PPh_3)Cl]_2$, where Cl is acting as bridging ligand.

The chapter five describes the reactions of $[RuCl_3(AsPh_3)_2-(CH_3OH)]$ and $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ with number of thiocarboxa(i)-mides such as EPH, ETH, ETOLH, PPH and TPH. The compound $[RuCl_3-(AsPh_3)_2(CH_3OH)]$, on stirring for 4-5 hr under dry nitrogen atmosphere, with EPH, ETH, ETOLH or TPH in chloroform and in the presence of dichloromethane yields the dimeric complexes of the formula $[RuCl_2(AsPh_3(ligand)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$. In the absence of dichloromethane in the process of isolation of the product with PPH, the complex obtained was $[RuCl_2(AsPh_3)(PPH)_2]_2$. These complexes were found diamagnetic at room temperature, hence +2 oxidation state of Ru was established. The +2 oxidation state of Ru in these complexes was again confirmed by e.s.r. studies. The dimeric nature of the complexes was proposed on the basis of molecular weight determination studies. The proton NMR spectra of the complexes except the complex with PPH exhibited a single sharp signal at δ 5.3-5.4 for the proton of dichloromethane. The NMR spectra of the complexes displayed all the characteristic signals of the ligands, apart from signals of aromatic protons of AsPh$_3$, but for NH proton. However, in case of complex with ETOLH, the NH proton resonance was observed at δ 11.0. The coordination site of the ligands was decided on the basis of careful inspection of shift in four thioamide bands in the i.r. spectra. The coordination through thiocarbonyl S was established in the complexes of EPH, ETH and ETOLH and through N in case of complexes with PPH and TPH. The $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ undergoes substitution reaction on refluxing for 3-4 hr with the

//ligands EPH, ETH, ETOLH, PPH and TPH in methanol and under dry nitrogen atmosphere. One PPh_3 molecule is substituted by one molecule of ligand, thus the complexes obtained were of the type $[(\eta^5-C_5H_5)RuCl(PPh_3)(ligand)]$.

In the last sixth chapter, the reactions of trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P, As) with the ligands EPH, ETH, PPH, EPTH and TPH are investigated. The chloroform solution of parent compound trans-$[Rh(CO)Cl(MPh_3)_2]$ and the ligand was refluxed for an hour under N_2, which resulted in the formation of $[Rh(CO)Cl(MPh_3)(ligand)]\cdot\frac{1}{3}CHCl_3$. In these compounds $\nu(C\equiv O)$ is unusually high in comparison to that of $[Rh(CO)Cl(MPh_3)_2]$. Tentative explanation has been offered in terms of enhanced π-acidity of thiocarboxa(i)mides and the presence of CO trans to these ligands. On the basis of i.r. the mode of coordination of the ligand was suggested. NMR spectra of some of the complexes showed the characteristic signals of respective ligand and $PPh_3/AsPh_3$. The NH proton could not be detected in NMR spectra.

The estimations of Pd, Pt, Ru and Rh have been made on atomic absorption spectrophotometer. Most of Rh(I) complexes showed only intraligand (IL) and/or charge transfer (CT) bands.

All the complexes have been assigned a tentative geometry based on their analytical, spectral and magnetic observations.

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3. R. Saheb, U.C. Agarwala and S.K. Dikshit, Indian J. Chem., 20A, 1196 (1981); 22A, 24 (1983); 22A, 1050 (1983); 23A, 204 (1984).

4. L.D. Dave, Cherian Mathew and Varughese Oommen, Indian J. Chem., 22A, 420 (1983).

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CONTENTS

Chapter I

INTRODUCTION

Object and Scope of the Work

In the recent past[1-5] much interest has been shown in the reactions of ligands containing secondary thioamide (HN-C=S) group with number of transition and non-transition metal ions in various oxidation states. Although the metal ion complexes with these ligands have long been known but the bonding site in such ligands could not be decided unequivocally based on i.r. spectral data as the reports on the assignment and the contribution from δ(NH), ν(C-N), ν(C=S) and δ(CH) to the thioamide bands I, II, III and IV differ significantly.[6-8] In addition, it has long been known that number of important biological processes involve metal ions which coordinate with a wide variety of ligands having sulphur, nitrogen and oxygen atoms as donor sites. Particularly HN-C=S groups not only play significant role in them but have very important pharmacological properties as well.[9-12] These ligands are usually polyfunctional in nature and are capable of trapping metal ions in an organic sphere. They have been found

to show antiviral, anticancer and antitumour activities[13,14] in the biological systems. In order to understand these biological processes, there has been an increasing interest in the design and syntheses of new model complexes of properties similar to ones found in the biological processes. Further, inspite of a large amount of work carried out to understand the coordinating nature of thioamide group, the donor properties of sulphur or nitrogen or simultaneous involvement of both sulphur and nitrogen, the position of ligands in spectrochemical and nephelauxetic series etc. have not yet been well understood. Although mono-thio- and dithio-β-diketones have been used as ligands with nearly all the metals and possess very interesting properties but very little work[15-17] has been done on the study of the effects on these properties if one changes CH group of R_1CXCH_2-$CX'R_2$ (X, X' = S, O; R_1, R_2 = substituents of wide variety) by a more electronegative atom like nitrogen.

The present work is an attempt to explore, at least partially, the following aspects:

(i) The chelating behaviour of the thioamide group containing ligands in general; (ii) the nature of metal-sulphur and metal-nitrogen linkage; (iii) the position of metals and the ligands in the nephelauxetic and spectrochemical series, (iv) stereochemistry and coordination number of the transition metal ions; (v) the stability of the square planar complexes with the ligands having delocalized π-electron system; (vi) relative importance of various

resonance and tautomeric forms of the ligand for different metal ions and their contribution to the electronic structure of resulting coordination compounds, and (vii) change in both chemical reactivity and structural properties of thiocarboxa(i)-mides and their complexes induced by alterations in the peripheral structure of the coordinated ligands.

Complexing behaviour of following ligands has been investigated:
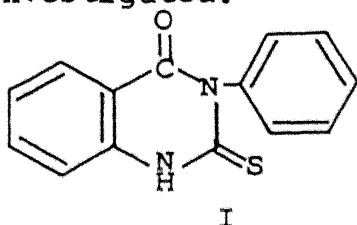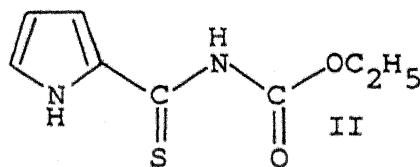
I

2-Mercapto-3-phenyl-
4-quinazolinone (MPQH)

II

N-Ethoxycarbonylpyrrole-
2-thiocarboxamide (EPH)

III

N-Ethoxycarbonylthio-
phene-2-thiocarboxamide
(ETH)

IV

N-Ethoxycarbonyltoluene-
4-thiocarboxamide (ETOLH)

V

N-Phenylcarbamoylpyrrole-
2-thiocarboxamide (PPH)

VII

2-Thiopyrrole-1,2-dicarb-
oximide (TPH)

$S=C-N-C-OC_2H_5$ VI
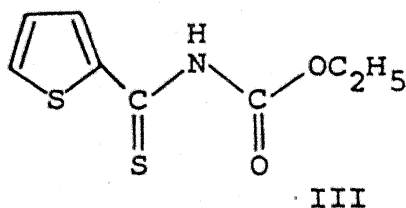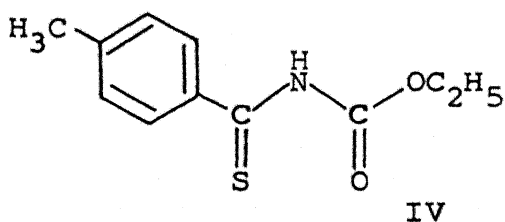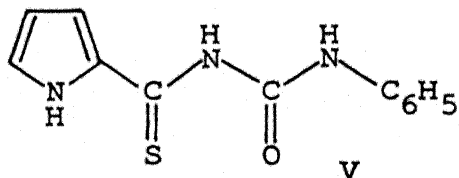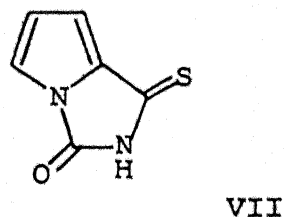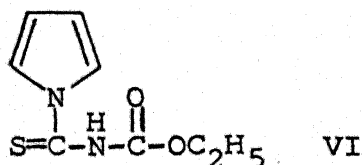
N-Ethoxycarbonylpyrrole-1-
thiocarboxamide (EPTH)

The metal ions which have been choosen for the study are: Mn(II), Co(II), Ni(II), Ru(II), Ru(III), Rh(I), Rh(III), Pd(II), Pt(II), Pt(IV), Cu(II), Ag(I), Pb(II), Cd(II) and Hg(II).

These ligands can act as mono, bi or polydentate towards one or more metal ions. The simultaneous participation of all the donor atoms for bond formation is virtually impossible because of electronic and stereochemical reasons. The stoichiometries, the oxidation state of central metal ions, the mode(s) of bonding and the geometries of the complexes have been found by chemical analyses, spectral studies (infrared, electronic, proton nmr, electron paramagnetic resonance), conductance and magnetic susceptibilities studies. Their possible structures have been tentatively proposed and given in Table I.1.

The metal-ligand bond will have partial ionic and partial covalent character which will vary within limits from bond to bond. The possibility of metal-ligand bond to be purely ionic or covalent is ruled out for the following reasons: (i) the metal and ligand coordinating atoms are of different size, (ii) they have different electronegativities, (iii) they have different polarizabilities. Besides σ-type of covalent bonds, there is possibility of π-bond formation ($d\pi - p\pi$ or $d\pi - d\pi$) in metal complexes (either $M \rightarrow L$ or $L \rightarrow M$). Since the overlap is considerably more effective along the internuclear axis than off it, π-bonds will be weaker than σ bonds and they do not generally exist independently. However, the formation of π-bonds will

tend to draw the nuclei involved closer together with a conse-
quent increase in the σ-overlap and hence an overall gain in
bond energy, resulting in the shortening of σ-bond. Further,
the formation of π-bond will also contribute towards reduction
in the mutual repulsions of the non-bonding electrons and thus,
strengthening the bond between metal and ligand. There is,
however, a controversy regarding back-bond formation. Thus, in
the complexes of phosphine or arsine, for example, the situation
is not clear and general opinion is against extensive π-back-
bonding.[18-20]

The strength and stability of a bond between the metal ion
and the donor atom would depend upon several factors like size,
electronegativity, the nature of orbital involved, their over-
lapping capacity etc. The number and the nature of the substi-
tuents attached to the ligand donor atoms will also influence
the stability of the bond between metal ions and donor atoms.

Since the identification of four thioamide bands and effect
on these bands after complexation is of prime importance in decid-
ing the bonding sites, it will not be out of place to give a brief
account of the interpretation of ir data.

Infrared spectra of organosulphur compounds have been
reviewed by Bellamy.[21] The frequencies ranging from 850 to
1550 cm^{-1} have been attributed to the C=S stretching frequency
in the literature[22] and there seems to be no adequate correla-
tion in the literature data. The uncertainty regarding assign-
ment of C=S stretching frequency has been examined by Rao and

Table I.1. Formula, structure, bonding scheme and colour of the complexes

Sl. No.	Complex	Structure	Bonding	Colour
1	2	3	4	5
1.	$Co(MPQ)_2(py)H_2O$	Octahedral (open polymeric)	A	dg
2.	$Co(MPQ)_2(\beta-pic)_2$	"	A	lb
3.	$Co(MPQ)_2(imzH)H_2O$	"	A	sg
4.	$Co(MPQ)_2(o-phen)$	"	A	oy
5.	$Co(MPQ)_2(pzH)$	Trigonal bipyramidal (open polymeric)	A	op
6.	$Ni(MPQ)_2(py)_2$	Octahedral (open polymeric)	A	g
7.	$Ni(MPQ)_2(\beta-pic)_2$	"	A	lg
8.	$Ni(MPQ)_2(imzH)H_2O$	"	A	gb
9.	$Ni(MPQ)_2(o-phen)$	"	A	lg*
10.	$Ni(MPQ)_2(bipy)$	"	A	yg
11.	$Ni(MPQ)_2$	Tetrahedral	A	lg*
12.	$MnO(MPQH)$	Suare planar (polymer)	B	b
13.	$MnO(MPQH)_2(py)$	Octahedral (polymeric)	B	b
14.	$MnO(MPQH)_2(\beta-pic)$	"	B	b
15.	$MnO(MPQH)_2(o-phen)$	"	B	b
16.	$MnO(MPQH)_{1/2}(bipy)H_2O$	Square pyramidal (polymeric)	B	b
17.	$Pd(MPQ)_2$	Square planar	A	o
18.	$Pd(MPQ)Cl(py)$	"	A	o

Table I.1 (contd.)

1	2	3	4	5
19.	Pd(MPQ)Cl(β-pic)	Square planar	A	by
20.	Pd(MPQ)Cl(o-phen)$_{1/2}$	"	A	oy
21.	Pd(MPQ)Cl(bipy)$_{1/2}$	"	A	y
22.	Pd(MPQH)Cl(imz)	"	A	y
23.	Pt(MPQ)$_2$	"	A	ly
24.	Pt(MPQ)$_2$(py)	Square planar or square pyramidal	A	y
25.	Pt(MPQ)$_2$(β-pic)	"	A	ly
26.	Pt(MPQ)$_2$(o-phen)$_{1/2}$	"	A	g
27.	Pt(MPQ)$_2$(bipy)$_{1/2}$	"	A	lb
28.	Pt(MPQ)$_2$(imz)Cl	Octahedral	A	gb
29.	Pt(MPQ)$_2$(pz)Cl	"	A	sg
30.	Pt(MPQ)$_2$(pyrm)$_{1/2}$	Square planar or square pyramidal	A	gb
31.	Ru(MPQ)$_2$Cl.DMF	Octahedral	B	v
32.	Ru(MPQ)$_2$Cl(H$_2$O).H$_2$O	"	B	b*
33.	Ru(MPQ)$_2$Cl(py).H$_2$O	"	B	gb*
34.	Ru(MPQ)$_2$Cl(β-pic).H$_2$O	"	B	bb*
35.	Ru(MPQ)Cl$_2$(o-phen).H$_2$O	"	B	rb
36.	Ru(MPQ)$_2$Cl(imzH).H$_2$O	"	B	sg
37.	Rh(MPQ)(MPQH)Cl$_2$.2H$_2$O	"	B	y
38.	Cu(ET)$_2$	Square planar	B	lg
39.	Ni(ET)$_2$(py)	Square pyramidal	B	b
40.	AgET	linear	N & O	y

Table I.1 (contd.)

1	2	3	4	5
41.	$Ru(ET)_2Cl(H_2O)$	Octahedral	B	v
42.	$[Rh(ETH)(PPh_3)Cl]_2$	Square planar	B	y
43.	$Rh(ET)_2Cl(H_2O)$	Octahedral	B	oy
44.	$Pd(ET)_2$	Square planar	B	oy
45.	$Pt(ET)_2$	"	B	db
46.	$[RuCl_2(AsPh_3)(EPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	Octahedral	C	b
47.	$[RuCl_2(AsPh_3)(ETH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	"	C	bv
48.	$[RuCl_2(AsPh_3)(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	"	C	dm
49.	$[RuCl_2(AsPh_3)(PPH)_2]_2$	"	D	rv
50.	$[RuCl_2(AsPh_3)(TPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	"	D	bv
51.	$(\eta^5-C_5H_5)RuCl(PPh_3)(EPH)$	Distorted octahedral	C	r
52.	$(\eta^5-C_5H_5)RuCl(PPh_3)(ETH)$	"	D	rv
53.	$(\eta^5-C_5H_5)RuCl(PPh_3)(ETOLH)$	"	C	yo
54.	$(\eta^5-C_5H_5)RuCl(PPh_3)(PPH)$	"	D	r
55.	$(\eta^5-C_5H_5)RuCl(PPh_3)(TPH)$	"	D	rv
56.	$[Rh(CO)Cl(PPh_3)(EPH)] \cdot \frac{1}{3}CHCl_3$	Square planar	C	gy
57.	$[Rh(CO)Cl(AsPh_3)(EPH)] \cdot \frac{1}{3}CHCl_3$	"	C	y

...contd.

Table I.1 (contd.)

1	2	3	4	5
58.	$[Rh(CO)Cl(AsPh_3)(ETH)]-$ $\cdot\frac{1}{3}CHCl_3$	Square planar	C	rb
59.	$[Rh(CO)Cl(PPh_3)(PPH)]-$ $\frac{1}{3}CHCl_3$	"	C	dy
60.	$[Rh(CO)Cl(AsPh_3)(PPH)]-$ $\cdot\frac{1}{3}CHCl_3$	"	D	y
61.	$[Rh(CO)Cl(PPh_3)(EPTH)]-$ $\cdot\frac{1}{3}CHCl_3$	"	C	yb
62.	$[Rh(CO)Cl(AsPh_3)(EPTH)]-$ $\cdot\frac{1}{3}CHCl_3$	"	C	rb
63.	$[Rh(CO)Cl(PPh_3)(TPH)]-$ $\cdot\frac{1}{3}CHCl_3$	"	D	dy*
64.	$[Rh(CO)Cl(AsPh_3)(TPH)]-$ $\cdot\frac{1}{3}CHCl_3$	"	D	yb

A, Ligand is acting as bidentate and bonded through thiocarbonyl sulphur and imide nitrogen atoms to two metal atoms.

B, Ligand is acting as bidentate, chelating ligand, bonded through sulphur and nitrogen atoms of the thioamide group to one metal atom.

C, Ligand is acting as unidentate and bonded through sulphur of the thioamide group.

D, Ligand is acting as unidentate and bonded through nitrogen of the thioamide group.

dg = dirty green; lb = light brown; sg = steel grey; oy = orange yellow; op = orangish pink; g = green; lg = light green; gb = greenish brown; lg* = light grey; yg = yellowish green; b = brown; o = orange; by = brown yellow; y = yellow; ly = light yellow; g* = grey; v = violet; b* = black; gb* = greenish black; bb* = brown black; rb = reddish brown; sg = sea green; db = dark brown; bv = bluish violet; dm = dark maroon; rv = reddish violet; dy* = dirty yellow.

Vankataraghavan,[23,24] who have carried out detailed correlation and have distinguished two groups of thiocarbonyl derivatives: the first group, where the thiocarbonyl group is linked to atoms such as carbon, sulphur, oxygen and chlorine; and the second group, where the thiocarbonyl group is linked to one or two nitrogen atoms. An unambiguous assignment of the C=S stretching frequency seems to be possible only when the C=S group is attached to atoms other than nitrogen. Similar observations were found by I. Suzuki,[25] he found that strong vibration coupling is operative in the case of nitrogen containing thiocarbonyl derivatives, the bands observed were interpreted on the basis of normal coordinate treatment.

Thiocarbonyl Derivatives, where the C=S group is linked to elements other than nitrogen

The C=S stretching frequency in thiofenchone is found around 1180 cm^{-1}. This is in fair agreement with the calculated frequency in thioformaldehyde.[26] The various thiocarbonyl derivatives for which the infrared data are available are ethylene-trithiocarbonate,[27,28] alkyl and perfluoroalkyl-trithiocarbonates,[29] thioesters,[30] 2,4-dihydroxy dithiobenzoic acid,[31] thiobenzophenones,[32] pyr-4-thione, 2,6-dimethylpyr-4-thione and thiopyr-4-thione,[33] pyrid-4-thione,[34] γ-mercaptoaza compounds,[35] alkyl and perfluoroalkyl chloroformates,[29] thiophosgene[31] and dianthogens and xanthates.[36,37] The assignments in these derivatives have been shown in the form of correlation Table I.2.

Table I.2. Correlation table

system	X	Y	ν(C=S) cm^{-1}
Ethylenetrithiocarbonate	S	S	1050–1075
Alkyltrithiocarbonate	S	S	1050–1100
Dithio esters	C	S	1160–1225
2,4-Dihydroxydithiobenzoic acid	C	S	1220
Thiofenchone	C	C	1170–1180
Thiobenzophenones	C	C	1210–1225
Pyr-4-thiones	C	C	1090–1160
Thiopyr-4-thione	C	C	1080–1090
γ-Mercaptoaza compounds	C	C	1090–1140
Alkyl dithiochloroformates	S	Cl	1070–1100
Thiophosgene	Cl	Cl	1115
Xanthate compounds	S	O	1010–1060

The C=S stretching frequencies in thiocarbonyl derivatives where the group is linked to elements other than nitrogen X and Y refer to the elements directly linked to the thiocarbonyl group

In case of xanthate compounds, the assignment in the range 1020-1070 cm^{-1} has been preferred. The assignments in region 1140-1265 cm^{-1} [37] probably corresponds to the C-O stretching vibration. The correlation clearly shows that the C=S stretching frequency in these derivatives falls within the range 1125 $\pm$ 100 cm^{-1}.

No simple correlation of the C=S stretching frequency with electronegativities of the atoms directly linked to the group is apparent. The linear relationship found by DAASCH[38] is not considered to be generally valid. In substituted phenyl derivatives[30,32] the C=S stretching frequency does not show any simple relationship with the Hammett σ or σ^+ constants of the substituents.[39] The thiocarbonyl group is not at all similar to the carbonyl group with regard to bond polarity and electrical effects of substituents.[28] The insensitivity of the thiocarbonyl stretching frequency to electrical effect is further confirmed by the fact that the calculated frequency of 1120$\pm$40 cm^{-1} for thioformaldehyde is not very different from the observed frequency of 1140 cm^{-1} for thiophosgene[26] and 1180 cm^{-1} for thiofenchone.

The only cases where the C=S frequency falls outside the limits of this correlation are xanthione, thioxanthione and N-methylthioacridone, all of which are heteroaromatic ketones. The C=S stretching frequency in these systems is found at 1330$\pm$30 cm^{-1}.[40]

Thiocarbonyl Derivatives, where the C=S group is linked to one
or two nitrogen atoms

Randall et al.[41] first observed that a strong band is
present in the region 1471-1613 cm^{-1} in the compounds where the
N-C=S unit is present. Several authors[42-45] have made a similar
assignments in a number of such systems. Subsequently it has
been shown by Elmore,[46] I. Suzuki[25] and many other workers that
this thioureide band results from the coupling of the C-N
stretching vibration and the NH deformation vibration. The
extreme variations in the assignment of the C=S stretching fre-
quency in the nitrogen containing thiocarbonyl derivatives is
undoubtedly due to vibrational coupling effect. In most of these
systems the C=S stretching vibration is not localised.

Suzuki has carried out extensive normal coordinate calcu-
lations of thioformamide, thioacetamide, N-methyl thioformamide
and N-methyl thioacetamide. The assignments of the observed bands
of thioformamide ($HCSNH_2$), thioacetamide (CH_3CSNH_2), N-methyl
thioformamide ($HCSNHCH_3$) and N-methyl thioacetamide ($CH_3CSNHCH_3$)
are given in Tables I.3 to I.5.

Characteristic Frequencies of Primary Thioamides

The observed band 1612 cm^{-1} of thioformamide was assigned
to almost pure $b(NH_2)$ bending vibration. This is in agreement
with the assignment by Davies and Jones.[47] In addition, there
is small contribution of the $\gamma(CN)$ mode.

Table I.3. Observed frequencies (in cm^{-1}) of thioacetamides (CH_3CSNH_2)

Solid	Liquid	Assignment
3290	3305	$\nu_a(NH_2)$
3165	3160	$\nu_s(NH_2)$
2945	2948	$\nu_a(CH_3)$
2860	–	–
2670	–	–
2620	2613	–
1648	1627	$b(NH_2)$
1478	1472	$\delta_a(CH_3)$
1392	1400br	$\nu(CN)$
1364	1364	$\delta_s(CH_3)$
1306	1302	skeletal + $r(NH_2)$
1030	1020	$r(NH_2) + r(CH_3)$
975	970	$\nu(CC) + r(CH_3) + \nu(CS)$
718	715	$\nu(CS) + \nu(CC)$
709	625br	$w(NH_2)$ & $t(NH_2)$
517	512	$\pi(CC)$
471) 460)	488	$\delta(NCS)$
375	373	$\delta(CC)$

Table I.4. The observed frequencies (in cm^{-1}) of N-methylthio-formamide (HCSNHCH$_3$)

Solid (-50°)	Liquid	Assignment
3160	3230	ν (NH)
3047	3047	–
2960	2985	ν_a(CH$_3$)
2850	–	–
1550	1537	ν(CN) + δ(NH)
1492	1479	δ_a(CH$_3$) + δ(CH) + δ(NH)
1470	1463	δ_a(CH$_3$) (A")
1440	1443	δ(CH) + ν(CN)
1392	1393	δ_s(CH$_3$)
1370	–	–
1308	1297	δ(CH) + δ(NH) + ν(CN)
1138	1136	r(CH$_3$) + ν(C'N)
	1010	π(CH)(A")
992	987	r(CH$_3$) + ν(C'N) + ν(CS)
985) 946)	–	–
912	920	–
874) 865)	868	ν(CS) + ν(C'N)
739	680	π(NH)(A")
	600	δ(NCS) –δ(CNC')
	467	–
	363	τ(CN)(A")
	(200)$_{calcd.}$	δ(NCS) + δ(CNC')

The band at 1443 and 1325 cm^{-1}. Davies and Jones assigned the 1443 cm^{-1} band of $HCSNH_2$ to $\nu(CN)$ vibration and 1325 cm^{-1} band to $\delta(CH)$ vibration. The Suzuki calculations establish that these two vibrational modes couple with each other almost completely and that of each the bands can not be assigned to a particular vibrational mode. The $\delta(CH)$ and $\nu(CN)$ vibrations also couple with each other in $HCONH_2$[48] but they are not so strong as in case of $HCSNH_2$.

The bands at 1125 and 843 cm^{-1}. The band at 1125 cm^{-1} of $HCSNH_2$ is chiefly associated with the rocking $r(NH_2)$ vibration although there is a small contribution from $\nu(CS)$ vibration. It is of general interest in the infrared investigation of thio-amides to determine in what region the frequency characteristic of the $\nu(CS)$ mode appears. Various authors indicate various regions for $\nu(CS)$ vibration,[44] e.g., $1500 - 1470$ cm^{-1}, around 1300 cm^{-1}, around 1100 cm^{-1} etc. In thiolactams, Mecke and Mecke[49] have assigned the band around 1100 cm^{-1} to this mode. In case of $HCSNH_2$, Davies and Jones indicated that the interaction probably occurs between the $\nu(CS)$ and $\nu(CN)$ modes and gives rise to two frequencies at 1443 and 1288 cm^{-1}. However, the 1288 cm^{-1} band is a weak shoulder of the strong 1325 cm^{-1} band and it can hardly be assigned to the one of the fundamental frequencies. These calculations also show that the 843 cm^{-1} band of $HCSNH_2$ corresponds to an almost pure $\nu(CS)$ mode, while there is a small contribution from the $r(NH_2)$ vibration to this band. It is true

that there are some difficulties in specifying the characteristic C=S frequency as suggested by Davies and Jones. The ν(CS) vibration interacts with several vibrational modes in CH_3CSNH_2, $HCSNHCH_3$ and $CH_3CSNHCH_3$ and it is rather hard to tell which band is to be called the C=S stretching band. However, in the case of $HCSNH_2$, the band at 843 cm^{-1} corresponds to almost pure ν(CS) vibration.

The band at 439 cm^{-1}. Suzuki's calculations show this band arises from the δ(NCS) vibration and corresponds well with the 412 cm^{-1} band of thiourea.

Characteristic Frequencies of Secondary Thioamides [N-methylthioformamide ($HCSNHCH_3$) and N-methylthioacetamide ($CH_3CSNHCH_3$)]

The nature of some vibration bands characteristic of the secondary thioamides will now be discussed in detail on the basis of assignments.

The band around 1550 cm^{-1}. The band at 1537 cm^{-1} of $HCSNHCH_3$ is assigned to the mixed vibration of the ν(CN) and δ(NH). The nature and the frequency of the band, as well as its change due to stage of aggregation, correspond to those of the amide II band in secondary amides.[50] In $CH_3CSNHCH_3$ this band is found at 1564 cm^{-1} in the solid state and at 1547 cm^{-1} in the liquid state. On N-deuteration, this band moves to a frequency

lower by about 30 cm^{-1}. Instead of δ(NH) vibration, the δ_a(CH$_3$) vibration couples with the ν(CN) motion in N-deuterated species; this gives rise to two frequencies at 1508 and 1438 cm^{-1} in HCSNDCH$_3$. In the case of CH$_3$CSNDCH$_3$, the δ_a(CH$_3$)$_C^*$ vibration also couples with ν(CN) vibration, as in the case of CH$_3$CSND$_2$ (II), the three frequencies are observed at 1515, 1483 and 1442 cm^{-1}.

The band around 1300 cm^{-1}. The band at 1297 cm^{-1} of HCSNHCH$_3$ is also assigned to the mixed δ(NH) and ν(CN) vibrations and corresponds to amide III band of mono substituted amides. However , the δ(CH) vibration also contributes to this band considerably. Although the spectra of N-methyl thioacetamides are complicated, it is quite probable that a strong band at 1261 cm^{-1} of the N-deuterated species corresponds to the band at 1238 cm^{-1} of CH$_3$CSND$_2$ (II) in its nature which is assigned to the composite vibration of skeletal stretching and deformation. In CH$_3$CSNHCH$_3$ a vibrational interaction certainly takes place between this skeletal and the δ(NH) modes, and the features of the vibration would resemble those of the amide III band. The amide III band occurs at 1299 cm^{-1} in CH$_3$CONHCH$_3$, which is about 50 cm^{-1} higher than that of HCONHCH$_3$. If we take the above facts into the account, the position of amide III like band of CH$_3$CSNHCH$_3$ is estimated at around 1350 cm^{-1} and probably overlaps the

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*In the CH$_3$CSNHCH$_3$, (CH$_3$)$_C$ and (CH$_3$)$_N$ are used to refer to the methyl group attached, respectively, to the carbon and nitrogen atoms.

$\delta_s(CH_3)_C$ band. This explains the lowering of bands in the carbon tetrachloride solution.*

The Skeletal Stretching Vibrations

As the value of force constants K_{CS}, K_{CC} and $K_{C'N}$ are close to each other, and interactions occur between the $\nu(C'N)$, $\nu(CS)$ and $\nu(CC)$ vibrations. Therefore, the nature of observed frequencies in the region $1100 - 800$ cm^{-1} becomes complicated. In addition, the $r(CH_3)_N$ and $r(CH_3)_C$ vibrations are also in this region.

Both $\nu(C'N)$ and $\nu(CS)$ vibrations take place in the normal modes of 987 and 868 cm^{-1} of $HCSNHCH_3$. The $r(CH_3)$ vibration also contributes to the former vibration. As for the 868 cm^{-1} band, the energy associated with the $\nu(CS)$ vibration is about 55% of the total and so this band may be called the $\nu(CS)$ band. In N-deuterated species, the $\delta(ND)$ vibration should also be taken into account, the band at 932 and 844 cm^{-1} are assigned to mixed vibration of the $\nu(C'N)$ and $\delta(ND)$, and of the $\nu(CS)$ and $\delta(ND)$, respectively.

In $CH_3CSNHCH_3$ three strong bands at 1099, 955, 684 cm^{-1} are assigned to the skeletal stretching vibration. The $r(CH_3)_N$ may also contribute considerably** to the 1099 cm^{-1} band. The

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*The intensity of the band becomes very strong.
**The band at 1099 cm^{-1} of $CH_3CSNHCH_3$ probably corresponds to those around 1100 cm^{-1} of thiolactams which are assigned to the $\nu(CS)$ vibration.[51]

band at 684 cm^{-1} corresponds to 718 cm^{-1} band of CH_3CSNH_2 and is certainly associated with the mixed mode of the $\nu(CS)$ and $\nu(CC)$ vibrations, of which the former is predominant. In N-deuterated species, the 956 cm^{-1} band is split into two bands at 990 and 930 cm^{-1}; the $\delta(ND)$ vibration probably takes place in both of these vibrations.

The NH out-of-plane Vibrations

The $\pi(NH)$ band is termed the amide V band in secondary amides and can easily be identified by its broadness and sensitivity to a change in states. In secondary thioamides it also occurs at about 680 cm^{-1} in the liquid state and on solidification moves to a frequency higher by about 60 cm^{-1}. The $\pi(ND)$ band is found about 500 cm^{-1}.

The Skeletal Deformation Vibrations

The band at 600 cm^{-1} of $HCSNHCH_3$ (and of $HCSNDCH_3$) is assigned to one of the skeletal deformation vibrations. The rather high frequency* of the deformation vibration is explained by the vibrational coupling of the $\delta(NCS)$ and $\delta(CNC')$ modes. In this vibration, the N-C=S angle increases while the C-N-C' angle decreases, or vice versa. In other words it corresponds to a

ɔf asymmetrical deformation vibration. Therefore the band

ɜponding to the "symmetrical" deformation falls at too low

$\delta(NCS)$ vibration usually occurs at about 450 cm^{-1} (I) and $\delta(CNC')$ at 350 cm^{-1}.[51]

a frequency to be detected.

In $CH_3CSNHCH_3$ the bands at 559, 374 and 287 cm^{-1} are assigned to the skeletal deformation vibrations. The 374 cm^{-1} band corresponds to the band at 378 cm^{-1} of CH_3CSNH_2 and is assigned to the $\delta(CC')$ vibration, while the other two are assigned to the to the "asymmetric" $\delta(NCS)$ and $\delta(CNC')$ and symmetric $\delta(NCS)$ and $\delta(CNC')$ vibrations, respectively.

It is heartening to find the adequate correlations between the three $-N-C=S$ bands, due to mixed vibrations in the regions 1395-1570 cm^{-1}, 1270 -1420 cm^{-1} and 940-1140 cm^{-1} in thiocarbonyl derivatives where $C=S$ group is linked to one or two nitrogen atoms, as suggested by Rao and Venkataraghavan and the assignments of Suzuki.

All primary thioamide show a band around 1620 cm^{-1} which is completely due to the NH_2 deformation vibration. In primary thioamide derivatives $-N-C=S$, I band is mostly due to C-N stretching. In thiourea, it is probably due to N-C-N asymmetric stretching. In secondary thioamides, NH deformation and C-N stretching constitutes the $-N-C=S$ I band. The thioamide II band in primary thioamide is due to mixed vibration involving CH deformation, C-N stretching, C-C stretching, NH_2 bending and $C=S$ stretching, depending on the nature of the compound. In secondary thioamides, $-N-C=S$ II band is mostly due to C-N stretching, NH deformation and CH deformation. In primary thioamides and in thiourea itself, thioamide III band is due to $C=S$ stretching and

NH_2 bending. The thioamide III band in secondary thioamides involves contribution from C-N stretching, C=S stretching and CH_3 bending.

Suzuki's studies indicate that in addition to thioamide bands I, II and III, all the nitrogen containing thiocarbonyl derivatives also show a band in the region 850-680 cm^{-1} due to mixed vibrations involving considerable contribution from C=S stretching. This band may be designated as the thioamide band IV.

The description of the -N-C=S IV band for some of the derivatives are shown below. On closer examination, one finds that many of the derivatives studied[23] earlier also show absorption in the region 900-670 cm^{-1} probably due to thioamide band IV.

Compound	Band position, cm^{-1}	Suzuki's assignment
Thioformamide	843	$\nu(C=S) + \nu(NH_2)$
Thioacetamide	718	$\nu(C=S) + \nu(CC)$
N-Methylthioformamide	868	$\nu(C=S) + \nu(CN)$
N-Methylthioacetamide	690	$\nu(C=S) + \nu(CC)$
Thiourea	732	$\nu(C=S) + \nu(NH_2)$

The thioamide bands in some of the nitrogen containing thiocarbonyl derivatives with their assignments are given below:

Compound	No. of derivatives	Thioamide band (position in cm^{-1})		
		I	II	III
Thiohydrazides	8	1545–1495	1325–1300	1050–1010
Thiatriazoline thiones	4	1495–1440	1340–1315	943–916
Thiourethanes	5	1507–1492	1341–1304	1134–1130
Isoperthiocyanic acid	1	1508	1307	1005
2-Mercapto-1,2,4-triazole	1	1502	1274	985

In case of thiourethanes (a), the thioamide band I in the region 1507–1492 cm^{-1} seems to show slight dependence of its

$$R-\!\!\bigcirc\!\!-\overset{\overset{H}{|}}{N}-\overset{}{\underset{OC_2H_5}{C}}=S \quad (a)$$
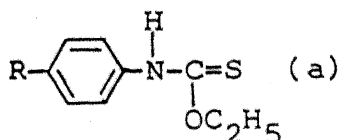
position on the electrical property of the parasubstituent. This may be probably due to the dependence of the Ph–N stretching vibration on the nature of the parasubstituent, since the transmission of electrical effects is through the Ph–N bond.

These four characteristic thioamide bands, namely band I ($\delta_{N-H} + \nu_{C-N}$), II ($\delta_{N-H} + \nu_{C-N} + \delta_{C-H}$) or ($\delta_{N-H} + \nu_{C-N} + \nu_{C=S}$), III ($\nu_{C-N} + \nu_{C=S}$) and IV ($\nu_{C=S}$) have been used to establish the coordination site(s) in many transition and non-transition metal complexes. Agarwala et al.[6] have studied the chelating behaviour of quinazoline (1H, 3H)-2,4-dithione with a number of metal cations viz. Co(II), Cu(II), Ni(II), Cd(II), Hg(II), Ru(II), Ru(III), Rh(I), Rh(II) and Rh(III) and modes of bonding were decided after careful study of the shifts of these four characteristic thioamide bands. Donor sites in the complexes of 1-substituted tetrazoline-5-thione complexes have been similarly identified.[7,8,52-54]

Eric S. Raper et al.[55-58] and many others have also utilised these characteristic thioamide bands for the determination of bonding. We have also utilized thioamide bands for ascertaining the mode of bonding.[59-63]

Table I.5. The observed frequencies (in cm^{-1}) of $CH_3CSNHCH_3$ (N-methylthioacetamide)

Solid	Liquid	Assignment
3207	3283	$\nu(NH)$
3077	3063	-
3019	-	-
2977	2985	$\delta_a(CH_3)_N$ & C
2935	2928	$\delta_s(CH_3)_N$ & C
1565	1547	$\delta(NH) + \nu(CN)$
1473	1460	$\delta_a(CH_3)_C$
1425	1438	$\delta_a(CH_3)_N$
1370	1360	$\delta_s(CH_3)_N$
1357	-	$\delta_s(CH_3)_C$ & $\nu(CN)$ + $\delta(NH)$
1243	1242	-
1211	1210	-
1099	1100	$\nu(CC) + \nu(CS) + r(CH_3$
1074	1060	-
1023	1020	$r(CH_3)_N$ & $r(CH_3)_C$
955	950	$\nu(C'N) + \nu(CS)$
746	690	$\pi(NH)$

...contd.

Table I.5 (contd.)

Solid	Liquid	Assignment
684	690	ν(CS) + ν(CC)
559	555	δ(NCS) - δ(CNC')
538	533	π(CC')
503	(503)	-
374	370	δ(CC')
387	(287)	δ(NCS) + δ(CNC')

ν = stretching; a = asymmetric; s = symmetric; δ = deformation; r = rocking; w = wagging, t = twisting; b = bending; π = out-of-plane bending; A" = out-of-plane vibration

A very brief review of the earlier work regarding the complexing behaviour of similar to title ligands is described in the following paragraphs.

(A) Thio-β-diketone

Holm et al.[64-67] have studied systematically the stereo-chemical and electronic effects of sulphur donor substitution in a variety of closely related chelate ligands of the type shown by I. By making comparisons among complexes identical in constitution except for the donor atom sets, the particular stereochemical consequences of sulphur ligation were assessed as follows:

$$R_1 \overset{H}{\underset{X}{\diagdown}} \overset{}{\underset{Y}{\diagup}} R_2$$
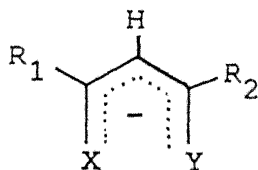
Ia, X = Y = O, β-diketone; Ib, X = O, Y = S, monothio-β-diketone;

Ic, X = O, Y = NR, β-ketoamine; Id, X = S, Y = NR, β-ketothione

(1) In general, unsaturated, sulphur containing chelate ligands may induce preferential stability of structures that are either unusual or of widespread occurrence. Thus sulphur tends to stabilize the planar form of monomeric complexes, particularly those of Ni(II) and Co(II). Examples include planar bisdithiolene[68] complexes and monothio-[69,70] and dithioacetylacetonates[71,72]. The trigonal prismatic structures of contain trisdithiolenes are unique to sulphur chelates.[68]

In the cases of nickel complexes of Ic and Id, measurements in noncoordinating solvents showed the presence of planar tetrahedral equilibria.[64,67] However, the equilibrium positions are such that the population of the planar isomer of the β-aminothione complex (Id) is always considerably greater than that of the β-ketoamine member (Ic) of the same pair. Thermodynamic measurements on these complexes confirmed that sulphur effects greater stabilization of planar stereochemistry than does oxygen and that the inequalities in stereochemical populations are due to enthalpy rather than entropy effects.[64] It was suggested that source of the stability differences of these isomers is associated with a larger extent of metal-ligand π bonding in the β-aminothiones, which can occur via ligand → metal

(HOMO $\rightarrow p_z$) and/or metal $\rightarrow$ ligand (d_{xz}^2, $d_{yz}^2 \rightarrow$ LUMO, $S d\pi$) electron transfer superimposed on the relative σ bond strengths.[64]

(2) For square planar monothio- -diketone complexes of nickel(II), palladium(II) and platinum(II), structural data have shown that only the cis isomer is formed.[73-78] Similarly, with the octahedral complexes of trivalent cobalt, vanadium, iron; ruthenium, and rhodium, NMR studies,[67] dipole moment measurements,[79,80] and X-ray results[81,82] all show that the cis (facial) arrangement is adopted exclusively. This preferential stability of the _cis_ form may arise in part from nonbonded S$\cdots$S interactions in the S_2 or S_3 units similar to those that have been suggested to assist in the stabilization of trigonal prismatic coordination.[83]

(3) Another structural consequence is depolymerization. Sterically unencumbered nickel(II) β-diketonates are trimeric in the solid state[84] and solution,[85] but similar NiO_2S_2,[69,70] $NiOS_3$,[86] and NiS_4[72,86] complexes are without exception monomeric and planar in both phases. Similarly, polymeric[87] cobalt(II) β-diketonates are degraded to simple CoO_2S_2[65] and CoS_4[72,86] monomers upon sulphur substitution.

Introduction of sulphur into the metal coordination sphere also promotes spin pairing. For example, while tris(acetylacetonato)iron(III) $[FeO_6]$ is high spin and the dithioanalog $[FeS_6]$ is low spin,[88] in ferric monothio-β-diketonates $[FeO_3S_3]$ exhibit spin isomerism to an extent dependent on the chelate ring substituents.[69,70] Donor atom dependence has also been observed in the

NMR spectra of thio-β-diketone complexes. Substitution of oxygen by sulphur causes a shift of both the methine and ring-substituent proton resonances to lower field.[86]

The mass spectrometric behaviour of the isostructural series of nickel complexes, bis(dipivaloylmethanido)nickel(II), and the monothio and dithio analogs has been studied.[89] It was observed that for the sequence $NiO_4 \rightarrow NiO_2S_2 \rightarrow NiS_4$, there was a marked decrease in the contribution of molecular ion peaks and, in general the percentage of the total ion current due to metal-containing peaks decreased in the order NiO_4 NiO_2S_2 NiS_4. The character of the spectra changed from one dominated by the fragmentation of the complexed ligands in NiO_4, to one dominated by fragmentation of the uncomplexed, oxidized ligands in NiS_4. This trend was observed in other similar complexes of both nickel and cobalt.[89]

A polarographic study[90] of above series of nickel complexes confirmed that substitution of oxygen by sulphur has both thermodynamic and kinetic consequences. As the number of sulphur atoms around the nickel atom increases, the reduction is easier (more positive $E_{1/2}$) and the heterogeneous electron transfer step is faster. This trend parallels that observed[91] for the ML_3 complexes of acetylacetone and dithioacetylacetone and for the NiLL' complexes of monothio- and dithioacetylacetone.

The consequence of gradual replacement of oxygen by sulphur is thus well illustrated by the series of complexes formed from

acetylacetone and its thioanalogs. The detailed information regarding ligation of monothio-β-diketone,[69,70,92] dithio-β-diketone[93,94] and related ligands is given in various reviews.

(B) Thiocarbamates

(i) Monothiocarbamate

The related dithiocarbamates have been under study for well over seventy years whereas the coordination chemistry of monothiocarbamate ligands has received attention only within the past ten years.

The most common synthetic procedure for N,N-disubstituted monothiocarbamate ligand involves the treatment of carbonyl sulphide, OCS, with a secondary amine to provide an ammonium salt[95-97] as shown in the Equation:

$$2\ R_2NH + OCS \longrightarrow [R_2NH_2]^+ [R_2NCOS]^-$$
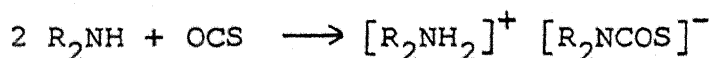
The majority of the studies have involved the following secondary amines: N,N-dimethylamine, N,N-diethylamine, N,N-dipropylamine, piperidine, pyrrolidine, indole, pyrrole, indoline. In general, the ammonium and alkali metal salts provide reasonable stable starting materials (when dry) for the synthesis of a wide variety of metal complexes.

Most of the complexes reported to-date have been prepared by the metathetical reaction of a monothiocarbamate salt with transition metal salt in a polar non-aqueous solvent. All the

complexes reported thus far involve ligands of the type $R_2NC(=O)S^-$ (R≠H). Metal dialkylamides have been shown[98,99] to react with OCS to form monothiocarbamates in what presumably is an insertion reaction:

$$M(NR_2)_4 + 4\ OCS \longrightarrow M(OCSNR_2)_4$$

(M = Th, U, Ti, Zr and R = Me, Et, i-Bu)

A unique and interesting procedure for the synthesis of $Fe(Me_2mtc)_3$ has been reported by Nakajuma et al.[100] Bis(N,N-dimethylcarbamoyl)-disulphide was reacted with $Fe_2(CO)_9$ to give what was thought to be $[Fe(Me_2mtc)_2]_n$ as an insoluble polymeric material. Oxidation of this material with elemental S or Se provided $Fe(Me_2mtc)_3$. Finally, the tin derivatives $Me_3Sn(R_2mtc)$ have been used as a starting material[101] for several organometallic complexes, as illustrated by the reaction:

$$Me_3Sn(R_2mtc) + Mn(CO)_5Br \longrightarrow Mn(CO)_5(R_2mtc) + Me_3SnBr$$

A few examples of well characterised complexes are $[Cu(Pr_2mtc)]_6$,[102] $[Zn(pipmtc)_2(pip)_2]$[103,104] (pip = piperidine), $Ti(Et_2mtc)_4$,[105] $(\eta^5-C_5H_5)[Mn(CO)_3Me_2mtc]_2$,[101] $(\eta^5-C_5H_5)Mo(CO)_2(Me_2mtc)$,[106] $Fe(Me_2mtc)_3$,[107] $[Co(pyrmtc)_2(pyr)_2]$[108] (pyr = pyrrolidine), $[Ni(R_2mtc)_2]_6$,[109] $[Pd(R_2dtc)(R_2mtc)]_2$, $(\eta^5-C_5H_5)_2U(Et_2mtc)_2$[110] and $Rh(MTC)_3Cl_3$ (MTC = N-methyl-O-ethylthiocarbamate). The structural studies reported todate unequivocally establish that there are at least four bonding modes, for monothiocarbamate

ligands, given below:
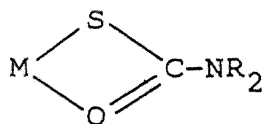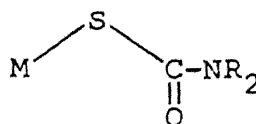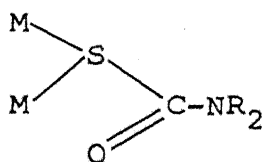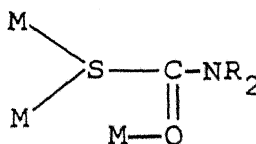
The monothiocarbamate ligand is bonded monodentately through sulphur to soft metal ions whereas it is bidentate to hard acids.[111] In all the reported structures the sulphur atom of the ligands are located cis. The appearance of $\nu(C\text{---}N)$ above 1545 cm^{-1} has been taken to indicate that the ligand is bonded monodentately through sulphur, values below 1545 cm^{-1} are considered to be characteristic of bidentate ligands. There are exceptions and structural inferences based solely upon ir data must be viewed with caution. IR, NMR spectral data and X-ray structural studies are indicative of the relative importance of canonical form II in the valence bond description of the electronic structure of monothiocarbamate ligands.
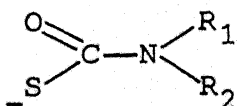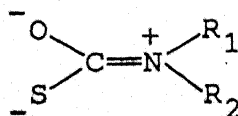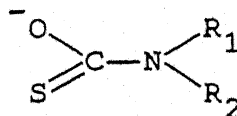
The relative importance of canonical forms I & III is diffi-
cult to assess. Based on electronegativity arguments one would
expect III, with negative charge residing on oxygen, to be more
important than I, with negative charge residing on sulphur. How-
ever, the chemical properties particularly the tendency of the
sulphur moiety to bridge, suggest that the sulphur donor has
considerable "mercaptide" character, consistent with form I.

Recently[112] some new organocobaloxime derivatives have been
synthesized by reaction of pyridinebis(dimethylglyoximato)cobalt(II)
with S-vinylmonothiocarbamates under H_2, in which (N,N-disubsti-
tuted) S-vinylmonothiocarbamates are attached to the Co-atom via
a Co-C σ bond. The chemistry of monothiocarbamates has been
recently reviewed by McCormic et al.[113]

(ii) Dithiocarbamate

These complexes have been extensively studied and some of
them commercially use as fungicides. Dithiocarbamates and their
analogous have two poential sulphur donor atoms joined to a
single C-atom and their complexes are some time called 1,1-dithio-
lato complexes. The bonding of dithiocarbamates is variable and
can function either as unidentate or bidentate (chelating) ligands:
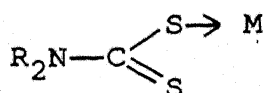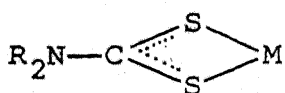
| Unidentate | Symmetrical chelate | Unsymmetrical chelate |
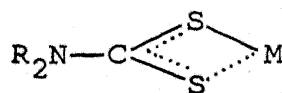
The unidentate and chelate types can be distinguished by ir and nmr spectra.[114] The nmr spectra of chelate dithiocarbamate groups are commonly temperature dependent due to dynamic processes involving nonequivalence of the R groups, rotation about the C-N bond, and for tris-chelates $M(dtc)_3$, intramolecular metal centred dynamic processes by a trigonal twist mechanism.[115] In chelating mode they frequently stabilize the metal centre in an unusually high apparent formal oxidation states, e.g., $[Fe^{IV}(S_2CNR_2)_3]^+$ and $[Ni^{IV}(S_2CNR_2)_3]^+$. They also have propensity for stabilizing novel stereochemical configurations, unusual mixed oxidation states, intermediate spin states (e.g., Fe^{III}, $S = 3/2$) and for forming a variety of tris-chelated complexes of Fe^{III} which lie at the $^3T_1 - {}^6A_1$ spin cross over.[116] The major forms for dithiocarbamate are:
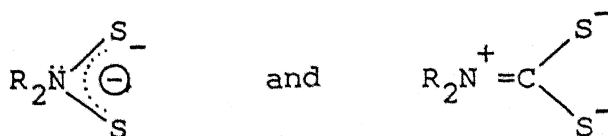
The NR_2 group has a strong electron releasing effect and when this is altered as in ligands such as:
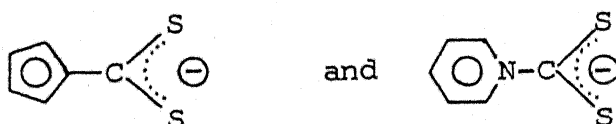
different behaviour towards metal can be achieved.[117,118] Thus in the cyclopentadienyl compound, the driving force tending to make the ring aromatic leads to a dominant π-acceptor character at sulphur.

Metal dithiocarbamates have been reviewed by Coucouvanis,[119] Eisenberg[120] and R.P. Burns et al.[121] and they presented comprehensive account of the work reported in the literature. There is, however, continuous interest in the synthesis, characterisation, electronic structure and bonding of these complexes. A few selected recently reports are cited below:

A series of seven coordinate $M(CO)_{3-n}L_n(S_2CNC_4H_4)_2$ (n = 0-2) molybdenum(II) and tungsten(II) complexes have been synthesized[122] with electronically unique pyrrole-N-carbodithioate chelating ligand: $[M(CO)_2L(S_2CNC_4H_4)_2$: M = Mo, W; L = PPh_3, PEt_3, $P(OMe)_3$; M = Mo; L = OC_4H_8, $AsPh_3$, $SbPh_3$, SC_4H_8; $M(CO)L_2(S_2CNC_4H_4)_2$: M = Mo, W; L = $P(OMe)_3$; M = Mo; L = PEt_3, $\frac{1}{2}Ph_2PCH_2CHPCH_2$; $[R_4N]$-$[M(CO)_2X(S_2CNC_4H_4)_2]$: M = Mo, W; X = F; M = Mo; X = Cl, Br, I].

$[M(RC\equiv CR)_2(S_2CNMe_2)_2]^{123}$ (M = Mo. or W), $[W(PhC_2H)_3(S_2CNMe_2)_2]^{124}$ and $[Fe(S_2CNR_2)XX']^{125}$ have recently been reported.

(C) Thiobiuret

$$RHN-\underset{\underset{X}{\parallel}}{C}-NH-\underset{\underset{X}{\parallel}}{C}-NHR' \quad (R,R' \text{ substituents; } X = O/S)$$
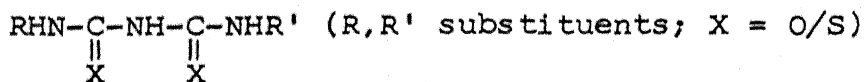
ML_2Cl_2 type of complexes (L = $NH_2CONHCSNH_2$; M = Co(II), Ni(II), Cd(II), Hg(II)) have been synthesized and their structures have been proposed on the basis of spectral (ir and electronic) and magnetic studies. The ligand is bidentate in Ni (trans-octahedral) and Cd (tetrahedral) complexes. In tetrahedral complexes of Co(II) and Hg(II), the ligand is unidentate.[126] Vanadyl(V) chloride forms $VOCl_3L$ with 1,5-disubstituted-2-thio-

biuret(=L) in CCl_4 solution. The ligand is bidentate through its S and O atoms.[127]

Many complexes of dithiobiuret and substituted dithiobiuret are known.[128-133] The complexes of Zn(II), Ni(II), Sn(II) and Cu(II) with substituted dithiobiuret (R = R' = Me, Et, morpholine) have been found[134] to be useful in population control, as insecticides and those of Ag(I), Cu(I), Ni(II), Pd(II), Hg(II), Fe(III), Zn(II), Cd(II), Cu(II) and Co(II)[135-139] with substituted dithiobiuret (R = Ph, R' = o-MeC$_6$H$_4$, p-MeC$_6$H$_4$; R = Me, R' = o-MeC$_6$H$_4$, p-MeC$_6$H$_4$) as fungicides. A few addition compounds[140-14] of Ni(NH$_2$CSNHCSNH$_2$)$_2$X$_2$ (X = Cl, Br, I, $\frac{1}{2}$ SO$_4$, CH$_3$OO) have also been isolated. The crystal structures[143] of two of the addition compounds Ni(NH$_2$CSNHCSNH$_2$)$_2$.glycol, Ni(NH$_2$CSNHCSNH$_2$)$_2$(ClO$_4$)$_2$.EtOH have been determined to investigate (a) The class of metal-ligand in neutral complex; (b) structural differences between neutral ligand complex and uninegative complex, and (c) the hydrogen bonded system in cationic complex.

The vanadium[144] dithioburet complex, $[(Cp)_2V(NH_2CSNHCSNH_2)]-[PF_6](Cp) = \eta^5-C_5H_5)$, has been reported and pseudotetrahedral structure has been assigned on the basis of IR, magnetic suscepti-bility, ESR, electronic spectra and molar conductance studies.

Gal et al.[145] reported the Rh and Pt complexes of dithio-biuret of general formulae Rh(CO)(PPh$_3$)L, Rh(PPh$_3$)$_2$L and PtH(PPh$_3$)L (L is bidentate and coordinated through both S). These complexes undergo reaction with oxygen giving 1:1 dioxygen adduct. In solu-tion trans-product of the complex Rh(PPh$_3$)$_2$(O$_2$)L has been observed.

Pignedoli et al.[146,147] have prepared and characterised number of 2,4-dithiobiuret (L) complexes of Zn(II), Cd(II) and Cu(I). In the complexes $Cd_2L_3Cl_4$, CdL_2X_2 (X = Br, I, ClO_4), $CdL_4(NO_3)_2$ and $CdL_3(SO_4).H_2O$. Ligand is monodentate and coordinated through one S atom, with a possible secondary weaker interaction of other CS group. The halide complexes were found non-conducting with bridging halide ligands while perchlorate complex in DMF is a 1:2 electrolyte. The nitrate and sulphate complexes are insoluble in DMF and probably have coordinated anions. CuLX (X = Cl, Br, I)[148] have been synthesized and characterized.

Sukhoruchkina et al.[149] studied the complexation of Cu(I) and Cu(II) with 2,4-dithiobiuret to determine the mechanism for Cu(II) catalysis of redox reactions between metal ions and 2,4-dithiobiret (BH). Amperometric, potentiometric and spectro-photometric studies indicate the formation of CuBCl at 1:1 Cu:HB ratio, but at 1:1.5 ratio, a redox reaction occurs, giving CuCl and the corresponding dithiazolidine. The dithiazolidine then forms a 1:2 Cu(I):ligand complex. Recently[150] Raman and IR spectra of 2,4-dithiobiuret (L), CuL_2Cl_2 and their deuterated derivatives were studied extensively by Jennings et al.

Tetramethyldithiobiuret ($Me_2NCSNHCSNMe_2$=L) reacts[151] with $Mo(CO)_3(\eta^5-C_5H_5)Cl$ in the presence of Et_3N to give the complex $[Mo(CO)_2(\eta^5-C_5H_5)(L^-)]$ with six membered ring.

The oxidative addition of unsaturated cyclic five membered disulphides to $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ resulted in the forma-tion of corresponding dithiobiuret complexes as given below.[152]

The reaction scheme shows:

Cl, PPh₃, Rh, Cl, PPh₃ with S, S, NMe₂, N, NMe₂ ← RhCl(PPh₃)₃ ← [central thiadiazolium cation with NMe₂, N, S⁺, S, NMe₂] Cl⁻ → Pt(PPh₃)₄ →

[Ph₃P, Pt, Ph₃P with S, S, Me₂N, N, Me₂N]⁺ Cl⁻, in CHCl₃ ,   [Cl, Pt, Ph₃P with S, S, NMe₂, N, NMe₂] in C₆H₆
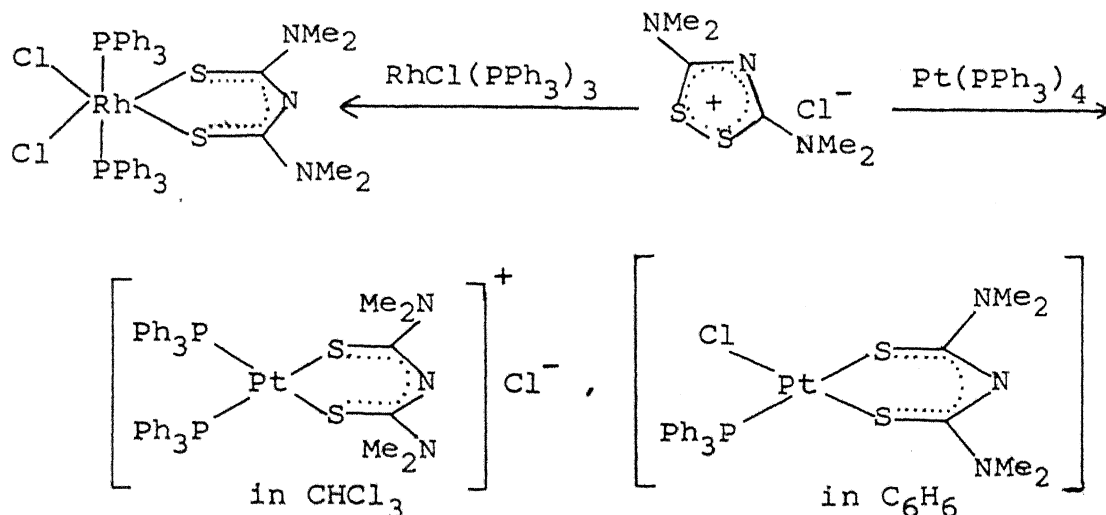
The reaction with $Pt(PPh_3)_4$ was found solvent dependent.

Mn(II) dithiobiuret complexes,[153] MnL_2SO_4 and $MnL_2X_2 \cdot EtOH$ (X = NCS, OAc) were prepared and characterised by IR spectra and thermal analyses. The ligand is bidentate with coordination through both S atoms, thus making the complexes octahedral, the sulphate group is in inner sphere whereas one of each OAc and NCS group is in outer sphere and the other is bridging.

Recently Fe(III) complexes of substituted dithiobiuret, $(FeCl_3L)_n$ (n = 1,2; L = RNHCSNHCSNHR'; R = R' = Ph, o-, p-tolyl; R = Ph, R' = o-, p-tolyl), have been reported. The dielectric constant and resistivity of these characterized complexes were studied as function of temperature. The data indicate possible transitions at 90 and 185° for monomers and dimers show no breaks.[154]

(D) Thiocarboxa(i)mides

The thiocarboxamides (RCSNHCOR') (R = 2-pyrrole; R' = OEt,

NHPh, NH_2) and thiocarboximides such as 2-thiopyrrole-1,2-dicar-
boximide and pyrrole-1,2-dithiocarboximide have been synthesized
E.P. Papadopouls[155] in 1973-74. These monothio-β-diketone type
ligands can function either as neutral or as anions with N, S
and oxygen as potential donors. Obviously their simultaneous
participation in complex formation would be virtually impossi-
ble. A study of metal complexes of N-ethoxylcarbonylpyrrole-2-
thiocarboxamide (EPH), N-carbamoylpyrrole-2-thiocarboxamide (CPH),
N-phenylcarbamoylpyrrole-2-thiocarboxamide (PPH), 2-thiopyrrole-
1,2-dicarboximide (TPH)[15-17] and pyrrole-1,2-dithiocarboximide
(PDH)[156] have been carried out to correlate the different physio-
chemical properties of the various metal complexes. Thus the
monomeric and polymeric forms of complexes of (EPH) and (PPH)
with the metal ions: Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II),
Cd(II), Pt(II), Pt(IV), Pd(II), Rh(I), Rh(III), Ru(II), Ru(III)
and Au(III); complexes of CPH and TPH with Cu(I), Cu(II), Ag(I),
Co(II), Ni(II), Ru(II), Rh(I), Pd(II) and Pt(II); complexes of
PDH with Fe(II), Ru(II), Co(I), Rh(I), Ni(0), Pd(0), Pt(0), Cu(I),
Ag(I) have been suggested.

The rare occurrence of Co(II) diamagnetic complexes with
the pyrrole derivatives as ligand have been explained by the
possible formation of δ-bond between two Co(II) ions present in
the square planar geometry. Different modes of bonding with
these ligands have been reported. The ligand as bidentate and
bonded through thiocarbonyl sulphur and carbonyl oxygen; acting
as unidentate and bonded through thioketosulphur; anionic and

neutral forms of the ligand; acting as bidentate towards two metal ions through nitrogen and sulphur atoms or both through nitrogen atoms.

In view of the potential interest in the complexing properties of the above mentioned ligands, the reactivity of similar ligands such as ETH, ETOLH and EPTH with several metal ions and their complexes have been described in this thesis. Recently, the reactions of $[Cu(MPh_3)_3X]$ (M = P, As; X = Cl, Br, I) with ETOLH were carried out which resulted in the formation of tetrahedral crystalline complexes of general formula: $[Cu(MPh_3)_2X-(ETOLH)]$ analogous with the compound $[Cu(PPh_3)_2Cl(TPH)]$ whose structure has been determined by X-ray diffraction method.[157] More studies on complexing behaviour of EtOLH and similar ligands are in progress in our laboratory.

As the present thesis also describes the complexing behaviour of 2-mercapto-3-phenyl-4-quinazolinone with several metal ions, it will be appropriate to review in short the earlier work in this field.

(E) <u>Quinazolin-2-thione-4-one</u>

A number of transition and non-transition metal complexes of 2-mercapto-3-(unsubstituted)-4-quinazolinone have been
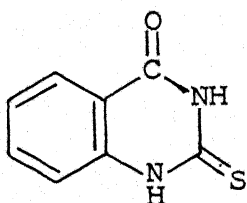
reported[8,158·161] but the ligating behaviour of 3-phenyl/substi-
tuted phenyl quinazolin-2-thione-4-one have not been much studied.
Only Cu(II) and Ni(II) complexes of 3-phenylsubstituted ligand
are reported.[162] They found anomalous paramagnetism of Ni(II)
complex (0.65 B.M.) and assigned it as due to temperature
independent paramagnetism. While we report here the formation
of high spin Ni(II) complex with the same ligand. The earlier
Cu(MPQ)$_2$ has been shown to be formed in solution conductometric-
ally.[163]

As the present thesis describes, also, the reactions of
$[(\eta^5$-C$_5$H$_5$)RuCl(PPh$_3$)$_2]$, $[$RuCl$_3$(AsPh$_3$)$_2$(CH$_3$OH)$]$ and trans-$[$Rh(CO)-
Cl(MPh$_3$)$]$ (M = P, As) with thiocarboxa(i)mides, a very brief
review of the earlier work regarding the reactivity of these
compounds towards other ligands is given in the following para-
graphs.

(A) $[(\eta^5$-C$_5$H$_5$)RuCl(PPh$_3$)$_2]$

The organometallic compound $[(\eta^5$-C$_5$H$_5$)RuCl(PPh$_3$)$_2]$ was
first prepared by Wilkinson (1969) and later was synthesized by
a facile route by Bruce and Windsor (1977), the pronounced steric
interaction and the presence of high electron density on ruthenium
resulting from two bulky tertiary-phosphine ligands linked to the
metal ion has possibly been responsible for its much unusual
chemistry. Further, the ready substitution of one of the PPh$_3$
molecules by other donor atoms and/or the ease of scission of

Ru-Cl bond in its methanolic solution has engendered an intense interest in its potential synthetic utility for the preparation of its large number of cationic and neutral substituted derivatives, thus making $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ as one of the most versatile organoruthenium(II) complex of contemporary interest.

The literature survey[164-178] reveals the excellent work of Bruce et al. where it has been shown that the complex $[(\eta^5-C_5H_5)-RuCl(PPh_3)_2]$ is the most attractive molecule for synthetic manipulation. Generally, two approaches have been applied to the syntheses of various complexes. One of them has centred around the reaction of the Ru-Cl bond resulting in the replacement of chlorine either by other anions or by neutral ligands to give cationic complexes of the type $[(\eta^5-C_5H_5)Ru(L)(PPh_3)_2]^+$ which is possibly based on the fact that the following reaction equilibrium lies largely on the right in its methanolic solution.[179]

$$[(\eta^5-C_5H_5)RuCl(PPh_3)_2] + CH_3OH \rightleftharpoons [(\eta^5-C_5H_5)Ru(CH_3OH)(PPh_3)_2]^+ + Cl^-$$
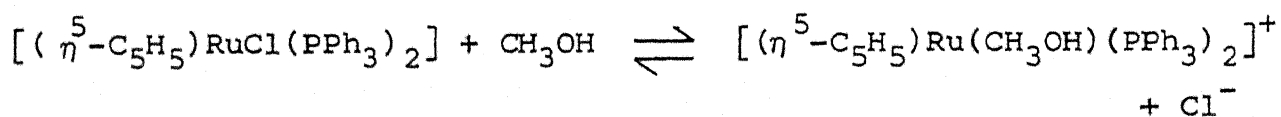
The second approach is based on the ready loss of one of the PPh_3 molecules, a feature of the reactions of the hydrides and alkyls, particularly with alkynes. In addition, there is also third possibility of the reactions, though very little studied, where C_5H_5 group could be activated towards substitution. The suggested factors for accounting these behaviours are: (a) the high electron density on ruthenium because of the presence of two

phosphine ligands[180] and (b) the steric interactions between the two bulky PPh_3 molecules. At present it appears from the structural analysis that there exists a highly crowded environment around phenyl rings not only in the triphenylphosphine complexes but also in the analogous complex[181] $[(\eta^5-C_5H_5)RuCl(PMe_3)_2]$.

The chloride ion in $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ can be replaced by other anionic group to give thermally stable complexes,[165,182] thus, the hydride is obtained by reacting the complex[183] with $LiAlH_4$. The complexes $[HRu(L)(L')(\eta^5-C_5H_5)]$ (L = PPh_3; L' = CO; $CNBu^t$, PPh_3, $P(OMe_3)$) are obtained by similar reaction.[184] In haloform the reactions of hydrides yielded the chlorides, and in CS_2, η^1-dithioformates, some of which curiously entered into chelation on heating as in the case of $[(\eta^5-C_5H_5)Ru(S_2CH)(PPh_3)]$.[184] The reactions of $NaBH_4$ with chloro complex gave grey white complex[185] of the type $[(\eta^5-C_5H_5)Ru(H_2BH_2)(PPh_3)_2]$ and the fluxional complex $[(\eta^5-C_5H_5)Ru(B_3H_8)(PPh_3)_2]$. The chloro atom of the complex is replaced by a number of pseudo-halides by facile metathetical reactions[179-182,186] to synthesize complexes $[(\eta^5-C_5H_5)-RuX(PR_3)_2]$ (R = Me; X = Br, I or SCN; R = Ph; X = CN). The cyanocomplexes which can be protonated or alkylated, also reacts with BPh_3 to give $[(\eta^5-C_5H_5)Ru(CNBPh_3)_2]$.[179] The bright yellow complex of trichlorostannate $[(\eta^5-C_5H_5)Ru(PR_3)_2(SnCl_3)]$ (R = Me, Ph)[165,186] is synthesized by inserting Tin(II) chloride into Ru-Cl bond.

The alkyl complexes $[(\eta^5-C_5H_5)Ru(PPh_3)_2(R)]$ are prepared by treating appropriate organolithium reagents[165] with

$[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$. Though the benzyl derivative is prepared using the Grignard,[169] the MeI gives only $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2I]$. By elimination of BPh_3 from some tetraphenylborate salts, the phenyl compound is synthesized.[179] The pentafluoro-analogue of the phenyl compound is obtainable by the reaction of of the chloro complex with LiC_6F_5.[165] Several types of reactions are employed to isolate the other unsaturated C-bonded ligands. For example, deprotonation of $[(\eta^5\text{-}C_5H_5)Ru(C(OR)CH_2R')(PPh_3)_2]^+$ with sodium methoxide affords the corresponding vinyl complexes $[(\eta^5\text{-}C_5H_5)Ru(C(OR)=CHR')(PPh_3)_2]$,[187] while a large series of σ-acetylides are obtained from $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ and HC_2R (R = Me, Pr, Bu^t, $(CH_2)_2C_2H$, Ph, $C_6H_4F\text{-}p$, C_6F_5, CO_2Me) by similar deprotonation of the intermediate vinylidene complex in situ.[172,173] On one instance (R = COMe), both reactions occur competitively, and both $[(\eta^5\text{-}C_5H_5)Ru(C_2COMe)(PPh_3)_2]$ and $[(\eta^5\text{-}C_5H_5)Ru(C(OMe)=CHC(O)Me)(PPh_3)_2]$ are formed.[187]

Recently[188] the reactions of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2X]$ (where X = Cl, Br, I, H, CN, NCS or $SnCl_3$) with N-donor heterocyclic bases like pyridine, picolines, 2,2'-bipyridine and 1,10-phenanthroline and with NOX (where X = Cl, Br, Br_3 or NO_2) have been carried out. The complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2X]$ (X = Cl or Br) on reacting with 2,2'-bipyridine and 1,10-phenanthroline gave cationic complexes as products, which were found to have composition, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(L)]^+X^-$ where L = bipy or o-phen and X = Cl or Br. The other complexes afforded neutral products of

composition $[(\eta^5-C_5H_5)Ru(PPh_3)(L)X]$ (where L = py, β-pic, γ-pic, $1/2$ bipy, $1/2$ o-phen ; X = Cl, Br, I, CN, NCS or SnCl$_3$). The hydrido complex $[(\eta^5-C_5H_5)Ru(PPh_3)_2H]$ which showed exceptional thermal stability, and reportedly undergoes a number of substitution reactions in a facile way, however, did not undergo ligand displacement reactions with N-donor ligands even under forcing reaction conditions. Interestingly α-picoline failed to give any isolable, stable reaction product.

The nitrosyl complexes of the type $[Ru(NO)(PPh_3)(L)XX_2']$ (where L = py, β-pic, γ-pic, $1/2$ bipy, $1/2$ o-phen; X = Cl, Br, I, CN or NCS; X' = Cl or Br) were isolated and characterized as the products of reactions of NOCl and NOBr with $[(\eta^5 C_5H_5)Ru(PPh_3)-(L)X]$. In the case of hydrido complex (X = H), the products were of composition $[Ru(NO)(PPh_3)_2YX_2]$ where Y = Cl, Br or I, depending on the haloform solvent used. The trischlorostannate complex, $[(\eta^5-C_5H_5)Ru(PPh_3)(L)(SnCl_3)]$ gave interestingly a nitrito complex, with a possible π-interaction of one of the phenyl rings of the PPh$_3$ ligand with Ru metal. The conversion of NO to NO$_2$ under mild reaction conditions with evidences of a vacant coordination site being blocked effectively by one of the phenyl rings of the PPh$_3$ in the case of trichlorostannate complexes is a fascinating one. In recent years, there has been considerable interest in the conversion of NO to the less harmful products N$_2$, N$_2$O, NO$_2$ and NH$_3$. This interest has largely stemmed from attempts to remove or atleast diminish the concentration of pollutant NO in exhaust gases emitted by

internal combustion engines.

The reactions of $NOBr_3$ afforded nitrosyl complexes of type $[Ru(NO)(PPh_3)(L)XBr_2]$ (where L = py, β-pic, γ-pic, 1/2 bipy, 1/2 o-phen ; X = Cl, Br, I, CN or NCS). In case of hydrido complex, $[(\eta^5-C_5H_5)Ru(PPh_3)H]$, the nitrosyl products are of composition, $[Ru(NO)(PPh_3)_2XBr_2]$ where X = Cl, Br or I, depending on the nature of the haloform used in the reaction mixture. The complex, $[(\eta^5-C_5H_5)Ru(PPh_3)_2(SnCl_3)]$ gave nitrito complexes which too show evidences of a π-interaction of one of the phenyl rings of PPh_3 ligand with Ru atom. The reactions of N_2O_3 with cyclopentadienyl complexes, gave nitrosyl dinitro complexes of type $[Ru(NO)(NO_2)(PPh_3)(L)X]$ including trichlorostannate complexes.

(B) $[RuCl_3(AsPh_3)_2(CH_3OH)]$

This compound was obtained[189] on refluxing ruthenium trichloride with excess of Ph_3As (6:1 mole ratio) in methanol. The presence of methanol was supported by the presence of methanol band in the region $1000 cm^{-1}$ in ir spectrum. This compound, on treatment with acetone, gave brown crystals of acetone complex $[RuCl_3(AsPh_3)_2(Me_2CO)]$ (ν_{CO} 1656 cm^{-1}) and with pyridine under very mild reaction conditions, gives the complex $[RuCl_3(AsPh_3)-(py)_2]$ suggesting that one of the Ph_3As group is comparatively labile, especially in the presence of ligands having a lower trans-effect. It also suggests that the Ph_3As groups are trans

to each other. Recrystallization[190] of methanol complex from
benzene or dichloromethane gives $[RuCl_3(AsPh_3)_2]$ which is a
discrete pentacoordinated monomer both in solid state and
solution.[191]

The substitution reactions of $[RuCl_3(MPh_3)(CH_3OH)]$ (M =
P, As) with whole range of nitrogen, oxygen and sulphur donor
ligands have been examined and, depending upon the conditions
and the nature of incoming ligands, various types of complexes
are formed:[190,192-194] (a) displacement of CH_3OH to give $[RuCl_3-$
$(MPh_3)_2L]$, (b) displacement of one MPh_3 and CH_3OH to give $[RuCl_3-$
$(MPh_3)L_2]$, (c) total displacement of one MPh_3 and CH_3OH, and
(d) reduction to ruthenium(II) with or without complete displace-
ment of MPh_3. The bromo analogue reacts in an essentially
similar manner.[190] mer-$[RuCl_3(PPhMe_2)_3]$ reacts with nitrogen
donors to give a related series of complexes.[192] Treatment of
$[RuCl_3(AsPh_3)_3]$ with R_4NCl gives the trans-octahedral[191,193]
anion $[RuCl_4(AsPh_3)_2]^-$, and with R_4NX (X = Br, I) mixed $[RuCl_3-$
$(AsPh_3)_2X]^-$ are obtained.[194] The reaction of $[RuL_2X_3]$ (L = PPh_3,
$AsPh_3$; X = Cl, Br) with hydrogen leads to the formation of the
pentacoordinated dimers $[Ru^{II}HXL_2]_2$, via the intermediates
$RuHX_2L_2$ and RuX_2L_2.[195] The reaction of $[RuCl_3(AsPh_3)_2(CH_3OH)]$
with cyclopentadiene[196] in the presence of zinc leads to
$[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$. The compounds $[RuCl_3(MPh_3)_2(CH_3OH)]$
(M = P, As) have been used as catalysts[197] in the homogeneous
reduction of 1-hexene to 1-hexane. Some of the Ru(II) complexes
containing tertiary-phosphine and arsine have been used as

catalysts for variety of reactions, including hydrogenation, oxidation, hydroformylation, hydration, polymerisation, carbonylation, decarbonylation, dehydrogenation, desulphonylation, isomerisation and alkylation. A review article[198] by B.R. James describes these reactions covering literature till 1969. Eventhough there has been extensive research carried out on ruthenium(II) tertiary phosphine and arsine complexes, the study on ruthenium(III) is relatively less.

Nyholm[199] et al. reported the preparation of Ru(III) complexes with o-phenylenebis(dimethylarsine) (DA). The complexes obtained were $[RuX_2(DA)_2][RuX_4(DA)]$ (X = Cl, Br) and $[RuX_2(DA)_2]\overset{.}{Y}$ (X = Cl; Y = Cl; X = Br; Y = Br; X = Cl; Y = ClO_4; X = I, Y = ClO_4). These complexes were prepared by oxidation of the Ru(II) complexes $[RuX_2(DA)_2]$ (X = Cl, Br) by chlorine and bromine. The ruthenium(III) carbonyl phosphine complex $[RuBr_3(CO)(PPh_3)_2]$ was prepared by Vaska[200] along with other ruthenium complexes $[RuX_3L_2 \cdot CH_3OH]$ (X = Cl, Br; L = PPh_3, AsPh_3).

The reactions of $[RuCl_3(AsPh_3)_3]$ with various ligands[201-203] lead the compounds of the type (i) $[RuCl_3(AsPh_3)_2L]$ (L = CH_3CH_2CH_2CN, CH_2=CHCN, DMF, CH_3CHO, C_6H_5CHO); (ii) $[RuCl_3(AsPh_3)L]$ (L = bipy, o-phen, (Me_2S)_2); (iii) $[RuCl_2(AsPh_3)_2L_2]$ (L = CH_3CN, CH_3CH_2CH_2CN, CH_2=CHCN) and (iv) $Me_4N[RuCl_3X(AsPh_3)_2]$ (X = Br or I). On the basis of the study of the electronic spectra of the complexes, an equilibrium between hexa- and penta-coordinated species in solution was postulated.

The reactions of $[RuCl_3(AsPh_3)_3]$ with K/Na thiocyanate and carboxylates gave $[Ru(SCN)_3(AsPh_3)_2]$ and $[RuCl_2(AsPh_3)_2(RCOO)]$ (R = CH_3, C_2H_5), respectively, while those with ammonia, amine and hydrazines gave Ru(II) complexes of the type $[RuCl_2(AsPh_3)_2L_2]$ (L = NH_3, CH_3NH_2, NH_2NH_2, $C_6H_5NHNH_2$). The reactions of β-diketones[202] with some of the ruthenium complexes, viz., $[RuX_3(MPh_3)_3]$ (X = Cl, Br; M = P, As) and $[RuBr_3(PPh_3)_2CH_3OH]$ gave compounds of the type $[RuX_2(bdk)(MPh_3)_2]$ (bdk = acetylacetonate, dibenzoylmethanate, benzoylacetonate; M = P, As; X = Cl, Br).

The compounds $[RuCl_n(PPh_3)(LH)_2]$ (n = 2, 3 ; LH = N-phenylcarbamoylpyrrole-2-thiocarboxamide) have been obtained as the products of reactions of $[RuCl_n(PPh_3)_3]$ (n = 2, 3) with LH.

The reactions of pyrrole-1,2-dithiodicarboximide (PDD) with $[RuCl_2(PPh_3)_3]$ and $[RuCl_3(AsPh_3)_2(CH_3OH)]$ afforded the complexes $[Ru(PDD)Cl_2(MPh_3)_2]$ (M = P, As), respectively similarly with N-sulphinylaniline (NSA), the compounds obtained were $[Ru(NSA)Cl_2(MPh_3)_2]$ (M = P, As).

(C) <u>trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P, As)</u>

The trans-$[Rh(CO)X(MR_3)_2]$ are well known and are formed from $[Rh(CO)_2Cl]_n$ and MR_3, $RhCl_3$ and MR_3 or $[RhCl_3(MR_3)_3]$ in alcoholic KOH and $[Rh(MR_3)_3X]$ and CO; the recent studies[204] have dealt with trans-$[Rh(CO)X(MR_3)_2]$ (X = Cl, occasionally Br, I; MR_3 = PPh_3, $AsPh_3$, $SbPh_3$, $PPhMe_2$, PCy_3, PMe_2Bz, $AsMe_2Bz$,

PMe$_3$, PEt$_3$, PPr$_3^n$, PBu$_3^n$, PPr$_3^i$, PBz$_3$, PPhEt$_2$, PPh$_2$Et, P(CH$_2$-SiMe$_3$)$_3$, AsPh$_2$Me, AsPh$_2$Et, P(p-tolyl)$_3$, AsCy$_3$, AsPh$_2$Pr^n, P(CH$_2$OCOMe)$_3$, PMe(CH$_2$OCOMe)$_2$, PEt(CH$_2$OCOMe)$_2$, PPh$_2$(CH$_2$OCOMe), PBu$_2^t$(CH$_2$OCOMe), P(CH$_2$OH)$_3$ and some cyclic phosphines.

The reaction of μ-dichlorotetracarbonyldirhodium, [Rh-(CO$_2$Cl]$_2$ with tertiary-phosphines has been extensively studied and some aspects of the work is included in a short review.[205] The system is unexpectedly complex and both mononuclear Rh(CO)$_{3-n}$Cl(PR$_3$)$_n$ (n = 1, 2, 3) and binuclear Rh$_2$Cl$_2$(CO)$_{4-m}$(PR$_3$)$_m$ (m = 0-4) have been identified in solution, although only certain members of each series can be isolated.[206] The reaction of [Rh(CO)$_2$Cl]$_2$ with PPh$_3$ in a 1:1 Rh:P ratio gives Rh$_2$(CO)$_2$-(PPh$_3$)$_2$Cl$_2$,[206,207] not trans-[Rh(CO)$_2$Cl(PPh$_3$)] as originally reported.[208] Subsequently other Rh$_2$(CO)$_2$(MR$_3$)$_2$Cl$_2$ (MR$_3$ = PMe$_3$, PPhMe$_2$, PEt$_3$, PCy$_3$, AsPh$_3$, SbPh$_3$ were prepared, the best general method being from [Rh(C$_2$H$_4$)(CO)Cl]$_2$ and MR$_3$ in a 1:1 ratio.[206-209] The reaction of [Rh(CO)$_2$Cl]$_2$ with triarylstibines[210] yields both red five and yellow four coordinated [Rh(CO)(SbR$_3$)$_3$Cl] and [Rh(CO)(SbR$_3$)$_2$Cl], depending upon the stibine used thus, Sb(o-tolyl)$_3$ yields only the four coordinate adduct, whilst the Sb(p-tolyl)$_3$ yields the four coordinate complex from cyclohexane and the five coordinate species from benzene. Triphenylstibine yields a mixture of [Rh(CO)(SbPh$_3$)$_n$Cl] (n = 2, 3), which are extremely difficult to separate[207,210] accounting for the variable properties reported in the literature. The reaction of Rh$_2$(CO)$_m$(C$_2$H$_4$)$_{4-m}$Cl$_2$ (m = 1 - 3) with R$_3$Sb produces various

mono and binuclear complexes in solution, but only the $[Rh(CO)-(SbR_3)_nCl]$ (n = 2, 3) can be isolated.[211]

We have synthesized the trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P, As) by the method reported by D. Evans et al.[212] from the reaction of $RhCl_3.3H_2O$ with two fold excess of arsine and formaldehyde solution.

Using ^{13}C and ^{31}P nmr it has been shown[213] that redistribution between $Rh(CO)(PR_3)_2Cl$ and $M(CO)(PR_3')_2Cl$ (M = Rh, Ir; R' ≠ R) is complete in a few seconds, probably via Cl-bridged dimers. Infrared intensity data[214] and ^{31}P nmr spectra trans-$[Rh(CO)(PR_3)_2X]$ have been reported.[214,215] Gray and coworkers[216] have recorded and interpreted the electronic spectra of trans-$[MX(CO)L_2]$ (M = Rh, Ir; L = PPh_3, $AsPh_3$, PEt_3, $SbPh_3$, and X = wide range of anions).

Halogen oxidation of trans-$[Rh(CO)(MR_3)_2X]$ yields[204] the corresponding $[Rh(CO)(MR_3)_2X_3]$ (X = Cl, Br). The reaction with nitromethane in DMF/H_2O converts $Rh(CO)(PPh_3)_2Cl$ into the iso-cyanate[217] $Rh(CO)(PPh_3)_2(NCO)$, which then reacts further with HBF_4 in alcohols to yield the carbamic ester compounds $[Rh(CO)(PPh_3)_2(OC(NH_2)OR)]$.

Both trans-$[Rh(CO)(MR_3)X]$ and $[Rh_2(CO)_2(PR_3)_2Cl_2]$ undergo numerous oxidative addition reactions with alkyl and acyl halides, etc., and form adducts with BX_3 and sulphur dioxide.[218] The work has been covered by the review.[219]

Sodium amalgam reductions of $[Rh(CO)(PPh_3)_2Cl]$ under carbon monoxide yields $[Rh(CO)_2(PPh_3)_2]^-$, from which penta-coordinated $RHg[Rh(CO)_2(PPh_3)_2]$ and $Hg[Rh(CO)_2(PPh_3)_2]_2$ can be obtained.[220]

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Chapter II

REACTIONS OF 2-MERCAPTO-3-PHENYL-4-QUINAZOLINONE WITH
Co(II), Ni(II), Pd(II), Pt(II) AND Pt(IV) IONS IN THE
PRESENCE AND ABSENCE OF VARIOUS N-HETEROCYCLIC BASES[*]

In this chapter, the syntheses and characterisation of the
mixed ligand complexes of Co(II), Ni(II), Pd(II), Pt(II) and
Pt(IV) have been described. The N-heterocyclic bases taken were
pyridine, β-picoline, 1,10-phenanthroline, 2,2'-bipyridine, imid-
azole, pyrazole and pyrimidine. Their structures have been pro-
posed on the basis of analytical, magnetic and spectroscopic (ir,
uv and visible) studies.

II.1 EXPERIMENTAL

All the chemicals used were either AR or chemically pure
grade. Palladium chloride and platinum chloride were purchased
from Sisco Research Laboratories (Pvt) Ltd., Bombay and used as
such. The ligand, 2-mercapto-3-phenyl-4-quinazolinone (referred
to as MPQH hereafter), was prepared by literature method.[1,2]

II.1.1   Preparation of 2-Mercapto-3-phenyl-4-quinazolinone

A mixture of equimolar quantities of phenyl isothiocyanate, C_6H_5NCS (6 ml) and anthranilic acid (6 g) in absolute alcohol (70 ml) was refluxed for 6 hr. The product was washed with ethanol, containing sodium hydroxide (10%, w/v), reprecipitated by HCl, filtered and washed several times with water and dried at 60-70°. The compound was recrystallized from hot ethanol. The colourless compound melts at 190°C.

II.1.2   Preparation of Metal Complexes

(i)   Aquabis(2-mercapto-3-phenyl-4-quinazolinonato)(pyridine)-cobalt(II), $[Co(MPQ)_2(Py)H_2O]$

An alkaline ethanolic solution (50 ml) of MPQH (1.06 g, 4 mmol) was added to an aqueous solution (40 ml) of $CoCl_2.6H_2O$ (0.476 g, 2 mmol) containing 5 ml of pyridine with stirring, followed by refluxing for an hour. The resultant dirty green precipitate was separated by filtration through sintered crucible, washed several times with water, ethanol and ether and dried in vacuo.

(ii)   Bis(2-mercapto-3-phenyl-4-quinazolinonato)bis(β-picoline)-cobalt(II), $[Co(MPQ)_2(\beta\text{-pic})_2]$

An alkaline solution (50 ml) of MPQH (1.06 g, 4 mmol) was added to an aqueous solution (40 ml) of $CoCl_2.6H_2O$ (0.476 g, 2 mmol) containing 5 ml of β-picoline with stirring, followed by

refluxing for an hour. The resultant light green precipitate
was separated by filtration through sintered crucible, washed
several times with water, ethanol and ether and dried in vacuo.

(iii) Aqua(imidazole)bis(2-mercapto-3-phenyl-4-quinazolinonato)
cobalt(II), [Co(MPQ)$_2$(imzH)H$_2$O]

An alkaline solution (50 ml) of MPQH (1.06 g, 4 mmol) was
added to an aqueous solution (40 ml) of CoCl$_2$.6H$_2$O (0.476 g,
2 mmol) containing 10 ml aqueous solution of imidazole (0.272 g,
4 mmol) with stirring, followed by refluxing for an hour. The
resultant steel grey precipitate was centrifuged, washed several
times with water, alcohol and ether and dried in vacuo.

(iv) Bis(2-mercapto-3-phenyl-4-quinazolinonato)(o-phenanthro-
line)cobalt(II), [Co(MPQ)$_2$(o-phen)]

An alkaline alcoholic solution (50 ml) of MPQH (1.06 g,
4 mmol) was added to an aqueous solution (40 ml) of CoCl$_2$.6H$_2$O
(0.476 g, 4 mmol) containing 15 ml of ethanolic solution of
1,10-phenanthroline (0.4 g, 2 mmol) with stirring, followed by
refluxing for an hour. The resultant orange yellow precipitate
was filtered off, washed several times with water, alcohol and
dried in vacuo.

(v) (Bipyridine)bis(2-mercapto-3-phenyl-4-quinazolinonato)-
cobalt(II), [Co(MPQ)$_2$(bipy)]

An alkaline ethanolic solution (50 ml) of MPQH (1.06 g,
4 mmol) was added to an aqueous solution (50 ml) of CoCl$_2$.6H$_2$O

(0.476 g, 4 mmol) containing 15 ml alcoholic solution of bipyridine (0.312 g, 2 mmol) with stirring, followed by refluxing for an hour. The resultant greenish brown precipitate was separated and washed several times with water, alcohol and ether and dried in vacuo.

(vi) Bis(2-mercapto-3-phenyl-4-quinazolinonato)(pyrazole)-cobalt(II), [Co(MPQ)$_2$(pzH)]

An alkaline alcoholic solution (50 ml) of MPQH (1.06 g, 4 mmol) was added to an aqueous solution (40 ml) of CoCl$_2$.6H$_2$O (0.476 g, 4 mmol) containing 15 ml ethanolic solution of pyrazole (0.272 g, 4 mmol) with stirring, followed by refluxing for an hour. The resultant orangish pink precipitate was separated by filtration through sintered crucible, washed several times with water, ethanol and ether and dried in vacuo.

(vii) Bis(2-mercapto-3-phenyl-4-quinazolinonato)nickel(II), [Ni(MPQ)$_2$]

An alkaline solution (50 ml) of MPQH (1.06 g, 4 mmol) was added to an aqueous solution (40 ml) of NiCl$_2$.6H$_2$O (0.476 g, 2 mmol) containing 5 ml ammonia solution with stirring, followed by refluxing for an hour. The light grey precipitate was centrifuged, washed several times with water, alcohol and ether and dried in vacuo.

(viii) Bis(2-mercapto-3-phenyl-4-quinazolinonato)bis(pyridine)-
nickel(II), [Ni(MPQ)$_2$(Py)$_2$]

Same as (i).*

(ix) Bis(2-mercapto-3-phenyl-4-quinazolinonato)bis(-picoline)-
nickel(II), [Ni(MPQ)$_2$(β-pic)$_2$]

Same as (ii).*

(x) Aqua(imidazole)bis(2-mercapto-3-phenyl-4-quinazolinonato)-
nickel(II), [Ni(MPQ)$_2$(imzH)H$_2$O]

Same as (iii).*

(xi) Bis(2-mercapto-3-phenyl-4-quinazolinonato)(o-phenanthroline)-
nickel(II), [Ni(MPQ)$_2$(o-phen)]

Same as (iv).*

(xii) (Bipyridine)bis(2-mercapto-3-phenyl-4-quinazolinonato)-
nickel(II), [Ni(MPQ)$_2$(bipy)]

Same as (v).*

(xiii) Bis(2-mercapto-3-phenyl-4-quinazolinonato)palladium(II),
[Pd(MPQ)$_2$]

A dimethylformamide solution (35 ml) of MPQH (0.508 g,
2 mmol) was filtered into dimethylformamide solution (20 ml) of

*An aq. solution of NiCl .6H$_2$O was used instead of cobaltous
chloride solution.

PdCl$_2$.2H$_2$O (0.214 g, 1 mmol). The solution was heated under reflux for 4 hr, and the resulting orange compound was centrifuged, washed with DMF, EtOH and Et$_2$O and dried at 80°C.

(xiv) General method of $[Pd^{II}(MPQ)Cl.B]$, (B = py, β-pic, (o-phen)$_{1/2}$ and (bipy)$_{1/2}$) and $[Pd^{II}Cl(imz)(MPQH)]$

A filtered alkaline (pH 9-10) alcoholic solution (25 ml) of the MPQH (0.254 g, 1 mmol) was added to hot aqueous solution (50 ml) of PdCl$_2$.2H$_2$O (0.214 g, 1 mmol) containing appropriate heterocyclic base* with stirring and the mixture was heated under reflux for an hour. The resultant precipitates were filtered, washed several times with water, alcohol and ether and dried at 80°C.

(xv) Bis(2-mercapto-3-phenyl-4-quinazolinonato)platinum(II), $[Pt(MPQ)_2]$

A solution of PtCl$_4$.5H$_2$O (0.427 g, 1 mmol) in H$_2$O (50 ml) was added to an alkaline EtOH solution (40 ml) of MPQH (0.508 g, 2 mmol). The mixture was heated under reflux for an hour, the yellow precipitate was then filtered off, washed several times with H$_2$O, not EtOH and finally with ether and then dried at 80°C.

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*5 ml pyridine, β-picoline; 5 ml alcoholic solution of 1,10-phenanthroline (0.1 g, 0.5 mmol). 5 ml alcoholic solution of 2,2'-bipyridine (0.08 g, 0.5 mmol) and 5 ml aqueous solution of imidazole (0.07 g, 1 mmol).

(xvi) General method for preparation of $[Pt^{II}(MPQ)_2.B]$ (B = py, β-pic, (o-phen)$_{1/2}$, (bipy)$_{1/2}$, (pyrm)$_{1/2}$), $[Pt^{IV}(MPQ)_2(imz)Cl]$ and $[Pt^{IV}(MPQ)_2(pz)Cl]$

An alkaline EtOH solution (40 ml) of the ligand MPQH (0.508 g, 2 mmol) was filtered into an aqueous solution (50 ml of $PtCl_4.5H_2O$ (0.427 g, 1 mmol) containing the appropriate heterocyclic bases* with stirring and heated under reflux for an hour. The resultant precipitates were centrifuged, washed with water, alcohol and ether and dried at 80°C.

II.1.3 Analyses

Estimation of cobalt and nickel[3]

A weighed amount of the complex was decomposed by digesting it with aqua regia for some time until the resulting residue gave a transparent solution when taken in dil. mineral acids. It was filtered and filtrate was made neutral if necessary. Cobalt was estimated in this solution by precipitating it with pyridine and ammoniumthiocyanate and subsequent weighing as $[Co(C_5H_5N)_4](SCN)_2$. Nickel was estimated by precipitating the solution with dimethylgloxime and weighing as $Ni(C_4H_7O_2N_2)_2$.

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*5 ml of pyridine, β-picoline; 5 ml alcoholic solution of 1,10-phenanthroline (0.1 g, 0.5 mmol); 5 ml alcoholic solution of 2,2'-bipyridine (0.08 g, 0.5 mmol); 10 ml alcoholic solution of pyrimidine (0.04 g, 0.5 mmol); 5 ml aqueous solution of imidazole, pyrazole (0.07 g, 1 mmol).

Estimation of palladium and platinum

Analyses of palladium and platinum were made on a IL-751 atomic absorption spectrophotometer. The sensitivity of this instrument for palladium is 0.14 μg/ml to 15 μg/ml (concentration of solution containing palladium metal) and for platinum 1 μg/ml to 150 μg/ml. In some of the complexes, the palladium was also estimated gravimetrically[3] as $Pd(dmg)_2$. The complex was decomposed by heating with mixture of H_2SO_4 and HNO_3.

Preparation of standard solutions for palladium analyses

0.00835 g of $PdCl_2.2H_2O$ was dissolved in 25 ml of distilled water containing a few drops of HCl and diluted to 100 ml. The concentration of palladium in this solution is 50 μg/ml. From 50 μg/ml solution, five standard solutions of concentration 1 μg/ml, 5 μg/ml, 7 μg/ml, 10 μg/ml and 15 μg/ml were prepared by diluting with distilled water. 25 ml of each standard solution is enough for analyses.

Preparation of sample solutions of palladium complexes

A weighed amount (4-6 mg) of the complex was decomposed by heating with mixture of HNO_3 and H_2SO_4 upto almost dryness, several times until the resulting residue gave clear solution in water. It was filtered and the filtrate was diluted with distilled water to a volume of 100 ml. The amount of the complex was taken in such a way that the concentration of Pd in its 100 ml solution lies in the range 1 μg/ml to 15 μg/ml.

Preparation of standard solutions for platinum analyses

The sensitivity of this instrument for platinum is 1 μg - 150 μg of platinum per millilitre. 0.034125 g of $(NH_4)_2PtCl_6$ was dissolved in 50 ml of distilled water and diluted quantitatively to a volume of 100 ml. The concentration of this solution is 150 μg of platinum per millilitre. On diluting this solution by distilled water, one can get the five standard solutions of concentration 30 μg/ml, 60 μg/ml, 90 μg/ml, 120 μg/ml and 150 μg/ml. 25 ml of each solution is enough for analyses.

Preparation of sample solutions of platinum complexes

A weighed amount (10-15 mg) of the complex was decomposed by heating with mixture of H_2SO_4 and HNO_3 upto almost dryness several times, until the resulting residue gave a transparent solution, when taken in about 15 ml of water. It was filtered and the filtrate was diluted to a volume of 25 ml by adding distilled water. The concentration of sample solution should be in the range of concentrations of standard solutions.

Estimation of halide and sulphur

For the estimations of halide and sulphur, the complexes were decomposed by fusing a weighed amount of complex with $NaNO_3$ and NaOH (8 and 64 times of the sample, respectively) in a nickel crucible for about 10 min. After cooling the crucible and extracting the residue with distilled water, the solution was filtered

and neutralised with dilute HNO_3 (in case of halide) or dil. HCl (in case of sulphur). Chloride was estimated as AgCl and sulphur, as $BaSO_4$ in the resulting solution.

Carbon, hydrogen and nitrogen were analysed by the Micro-analytical Section of the Indian Institute of Technology, Kanpur.

Infrared spectra

IR spectra of the ligand and metal complexes were recorded with a Perkin-Elmer 580 diffraction grating infrared spectrophoto-meter in the range 4000-200 cm^{-1}. Samples were prepared as KBr pellets.

UV-Visible spectra

The solid reflectance spectra of the complexes and absorption spectra of MPQH in DMF were recorded in the region 700-200 nm on Cary-17D UV-Visible spectrophotometer.

Melting points

Melting points of the complexes were recorded on a Fisher-John's melting point apparatus and are uncorrected.

Magnetic susceptibility measurements

Magnetic susceptibilities of the complexes were measured by a parallel field vibrating sample magnetometer (VSM) model-150A at 293 K.

II.2   RESULTS AND DISCUSSION

Analytical data as listed in Tables II.1 and II.2 are con-
sistent with the stoichiometry proposed for complexes.   All the
complexes are sparingly soluble in water and common organic sol-
vents.

The infrared spectrum of ligand MPQH showed a very complex
pattern of bands.   However, the spectrum was partially analysed
to get some information regarding the mode of bonding of metal
ions with the ligand.   It is well known that the organic compounds
containing thioamide group (H-N-C=S) give rise to four characte-
ristic thioamide bands[4,5] in the region 1500, 1300, 1000 & 800 cm^{-1},
respectively.   The careful analyses of the spectra of ligand and
the complexes, indicated that the four strong bands at 1540, 1345,
1000 (also 980) and 770 cm^{-1} may be taken as four characteristic
thioamide bands I, II, III and IV, respectively.   Positions of
these bands shift after complexation.

The i.r. spectrum of 2-mercapto-3-phenyl-4-quinazolinone
(MPQH) in solid state displays γ(NH) absorption band at ca. 3250
cm^{-1} but no absorption at ca. 2500 cm^{-1}, indicating that in the
solid state the compound exists as the thione (I) and not as
thiol (II) tautomer.   The relative low frequency of NH vibration
can be interpreted as arising of hydrogen bonding between the NH
and C=S group.[6]
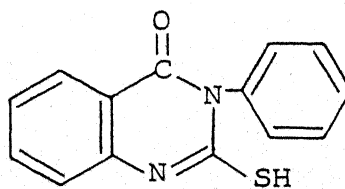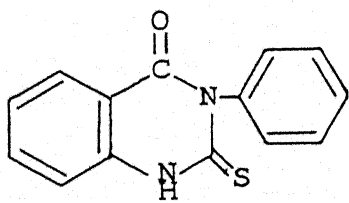
The strong band at 1660 cm^{-1} is assigned to $\nu(C=O)$. The $\nu(C=S)$ could not be assigned because of the strong coupling among $\nu(CN)$, $\delta(CH)$, $\nu(CS)$ and $\delta(NH)$ bands as discussed in Chapter I.[7]

II.2.1 IR Spectra

Co(II) and Ni(II) complexes of MPQH

The comparison of i.r. spectra of the MPQH and complexes reveals the following facts (Table II.3):

(i) The disappearance of the $\nu(NH)$ band of the ligand at 3250 cm^{-1} from the spectra of the complexes indicates the formation of Co-N/Ni-N bond, respectively.

(ii) The $\nu(C=O)$ band of the MPQH at 1660 cm^{-1} almost remains stationary or shifts to higher wave number in the spectra of the complexes. Thus the coordination through carbonyl group is ruled out in the complexes. Although C=O in conjugation with phenyl group poses difficulty in its assignments yet above inference is more likely as this band has major contribution from $\nu(C=O)$.

(iii) Thioamide band I (at 1540 cm^{-1}) and II (at 1345 cm^{-1}) of the ligand, having contribution from $(\delta_{N-H} + \delta_{C-H} + \nu_{C-N})$ and $(\nu_{C\cdots S} + \delta_{C-H} + \nu_{C\cdots N} + \delta_{NH})$, respectively shifted to lower wave number in the spectra of the all complexes. This indicates the simultaneous coordination through nitrogen and exocyclic sulphur atom.

(iv) The thioamide band III ($\nu_{C\cdots N} + \nu_{C\cdots S}$) is relatively weak in the spectra of the complexes.

(v) The thioamide band IV ($\nu_{C\cdots S}$) either shifted to lower wave number or splits in the spectra of the complexes. This again supports the involvement of sulphur atom in coordination.

(vi) In the spectra of complexes, there seems to be extensive mixing between the bands of the ligand and those of the bases,[8-11] hence characteristic frequencies of nitrogen heterocycles did not occur at their standard positions. However, bases are definitely coordinated in the complexes as some of the characteristic bands can be identified with small shifts. The band at 630 cm^{-1} in pyridine complexes is assigned to in-plane ring deformation shifted to higher frequency after complexation. Similarly bands at 1580 cm^{-1} (β-picoline, ν aryl C=N), 1580-1590 (bipyridine and phenanthroline, ν aryl C=N) indicate the coordination of respective bases.

(vii) New bands of medium intensity in the region 250-400 cm^{-1} appearing in the spectra of the complexes could be assigned to ν(M-N) and ν(M-S) modes of vibration.

(viii) The strong sharp band at 3580 cm^{-1} in the spectra of [Co(MPQ)$_2$(pzH)] may be assigned to ν(N-H) of pyrazole[12] & it seems to be coordinated to metal ions through its imino-nitrogen atom.

(ix) The broad band in the region 3300-3500 cm^{-1} in two complexes (Table II.3) may be assigned as mixed band of ν(N-H) of imidazole and water.

Pd(II), Pt(II) and Pt(IV) complexes (Table II.4)

The disappearance of ν(NH) of imidazole[13] and pyrazole from the i.r. spectra of $[Pt^{IV}(MPQ)_2(imz)Cl]$ and $[Pt^{IV}(MPQ)_2-(pz)Cl]$ and $[Pd^{II}(MPQH)(imz)Cl]$ indicates the deprotonation of the bases and bonding through N-atom of heterocycles. The absence of ν(N-H) at 3250 cm^{-1} from the spectra of all complexes except $[Pd(MPQH)(imz)Cl]$ indicates the displacement of the N-H hydrogen by Pd(II), Pt(II) and Pt(IV) and possible formation of metal nitrogen bond. The presence of a broad band at 3240-3260 cm^{-1} in the spectrum of $[Pd(MPQH)(imz)Cl]$ indicates that the ligand is coordinated as MPQH. The broadening of (NH) after complexation can be tentatively assigned to M-N bond formation.

The ν(C=O) band of MPQH at 1660 shifts towards higher wave numbers by 20-55 cm^{-1} in the spectra of the complexes; indicating the noninvolvement of C=O group in metal bonding

The thioamide band I either shifts to lower wave number or splits upon complexation. This observation supports the M-N bond formation. The thioamide band II splits as a result of coordination, probably because of simultaneous involvement of N and S in coordination. In the spectrum of $[Pd(MPQ)Cl(Py)]$, the band II shifts to lower wave number by 10 cm^{-1} and is of low intensity. The thioamide band III is relatively weak in the spectra of the complexes. The thioamide band IV $(\nu_{C\cdots S})$ of MPQH at 770 cm^{-1} either changes its position by ± 10 cm^{-1} or splits in the spectra of the complexes.

A red shift of 25-55 cm^{-1} in band IV usually indicates bonding through sulphur, and a blue shift of 40-90 cm^{-1} in this band, bonding through nitrogen. However, if there is simultaneous bonding through sulphur and nitrogen, there may not be much shift in band IV. Hence the above observation is attributed to simultaneous coordination through sulphur and nitrogen.

New bands of weak to medium intensity in the region 250-500 cm^{-1} in the spectra of the complexes are assigned to coupled vibrations, ν(M-Cl), ν(M-N) and ν(M-S).[14]

Characteristic frequencies of nitrogen heterocycles[8-11] were not present at their standard positions and could not be identified.

II.2.2 Electronic Spectra of the Complexes

Electronic spectrum of MPQH in DMF exhibits one strong transition band at 295 nm and one weak shoulder at 262 nm which are assigned to a $\pi \rightarrow \pi*$ intraligand (IL) transition.[15] The reason for not assigning as $n \rightarrow \pi*$ is that usually $n \rightarrow \pi*$ transition involving N and S atom occur at lower energy and are less intense.

Owing to the low solubility of the complexes, their electronic spectra were recorded in solid state. The band positions and their assignments are given in Tables II.5 and II.6.

Reflectance spectra of Co(II) and Ni(II) complexes

The electronic spectra of the complexes were interpreted on the assumption of high spin octahedral[16] geometry of all Co(II) and Ni(II) complexes except $[Co(MPQ)_2(pzH)]$ and $Ni(MPQ)_2$.

Very weak broad band around 600 nm in some of the Co(II) complexes may be assigned to ν_2 $[^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)]$ and weak shoulder around 500 nm in the spectra of complexes was assigned to ν_3 $[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$. However, ν_1 $[^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ could not be observed in the near IR spectrum of Co(II) complexes. In some cases most of d-d transitions were masked by strong charge transfer and intraligand transitions.

Similarly in the spectra of Ni(II) complexes, ν_2 and ν_3 transitions were observed as weak broad shoulder and assigned as given in Table II.5. ν_1 $[^3T_{2g}(F) \rightarrow {}^3A_{2g}(F)]$ could not be observed. The broad band at 250 nm and weak broad band around 300 nm (in MPQH, 295 nm) appeared in the spectra of the complexes may be assigned to intraligand charge transfer $L(\pi) \rightarrow L(\pi^*)$ transition (IL).[17]

Another weak shoulder appeared between 375-395 nm in some of the complexes is probably due to charge transfer (CT) $M \rightarrow L$ or $L \rightarrow M$ transition.

$Ni(MPQ)_2$ exhibited a weak shoulder at 680 nm apart from CT and IL bands which may be assigned as ν_3 $[^3T_1(F) \rightarrow {}^3T_1(P)]$ assuming the tetrahedral geometry of the complex.

UV-Visible spectra of Pd(II), Pt(II) and Pt(IV) complexes in solid state

The electronic spectra of these complexes exhibit almost continuous absorption in the region 700-360 nm. The d-d transitions in some of the complexes are probably masked by this continuous absorption or by strong charge transfer (CT) transitions. However, the spectra of some of the palladium and platinum complexes exhibited maxima at 410-440 nm (in Pd complexes) and 370-375 nm (in Pt complexes) which may be assigned to a d-d, $d_{x^2-y^2} \rightarrow d_{xy}$ ($^1A_{1g} \rightarrow {}^1B_{1g}$) transition for square planar complexes. A shoulder at ca. 320-355 nm in the spectra of complexes is assigned to a M $\rightarrow$ L or L $\rightarrow$ M charge transfer transition. Another shoulder at 285-300 nm is assigned to an intraligand (IL) $\pi \rightarrow \pi*$ transition.

It is also possible to derive[18,19] from the first allowed d-d transition the value of splitting parameter $\Delta_1 = \nu_1 + 3.5 \ F_2$ by assuming $F_2 = 10 \ F_4 = 600 \ cm^{-1}$ for the Slater-Condon interelectronic repulsion parameter of these complexes.

II.2.3 Magnetic Properties of the Complexes

All the compounds of Pd(II), Pt(II) and Pt(IV) were found diamagnetic at room temperature.

The magnetic susceptibilities hence magnetic moments of the complexes of Co(II) and Ni(II) were measured at room temperature and the calculated magnetic moments (in B.M.) of compounds are given in Table II.1.

In present study, the compound of known weight (5 to 15 mg) was filled tightly in small glass preferably quartz, capillary (2-3 mm outer diameter and 5-6 mm in length) and the magnetisation, M was measured at different field, H (1-10 kG). The M vs H plot gave a straight line, the magnetic susceptibility, X, was obtained from the slope of the line. The X_M can be calculated as

$$X_M = \frac{X \times Molecular\ Weight}{The\ Amount\ Taken\ (in\ g)}$$

The magnetic moments of the cobalt complexes except that of $[Co(MPQ)_2(pzH)]$ were found to be 4.7-4.9 B.M. (Table II.1) which are in good agreement with high spin octahedral complexes. The magnetic moment (4.25 B.M.) of $[Co(MPQ)_2(pzH)]$ suggest its probable geometry as trigonal bipyramidal.[20] Similarly magnetic moments (3.02 - 3.17 B.M.) of nickel complexes except $[Ni(MPQ)_2]$ are in good agreement with reported high spin octahedral nickel complexes. The magnetic moment (3.74 B.M.) of $Ni(MPQ)_2$ may be assigned to tetrahedral Ni(II) complex.

Thus on the basis of analytical, magnetic and spectroscopic data, the following geometries are tentatively proposed for the complexes. In the complexes of type $[PtL_2B]$, squar planar geometry is assigned on the assumption that one of the two ligands is a unidentate ligand, coordinated through nitrogen of the thio-amide group. The possibility of pentacoordination[21] in $[PtL_2B]$ is also not ruled out. The bidentate heterocyclic bases possibly function as bridging ligands.[22]

$[Co(MPQ)_2(pzH)]$ –   Trigonal bipyramidal

$[Ni(MPQ)_2]$ –   Tetrahedral

Remaining other)
Co(II) & Ni(II))   –   Octahedral
complexes)

$[Pd(MPQ)_2]$ –   Square planar

$[Pt(MPQ)_2]$ –   Square planar

$[Pt(MPQ)_2(imz)Cl]$ –   Octahedral

$[Pt(MPQ)_2(pz)Cl]$ –   Octahedral

Remaining other)
Pd(II) & Pt(II))   – ·   Square planar or square pyramidal
complexes)

In view of strain involved in four membered ring, if one assumes the ligand MPQH, acting as bidentate toward one metal atom and forming four membered chelate, open polymeric structure is preferred. Although this inference has been drawn, several four membered chelate rings are known with N, S ligands and the large size of the sulphur atom reduces undue strain of the ring.[23] As the complexes are sparingly soluble in most of the organic solvents, polymeric nature of compounds seems to be almost certain. The structure of the polymeric unit is given below:
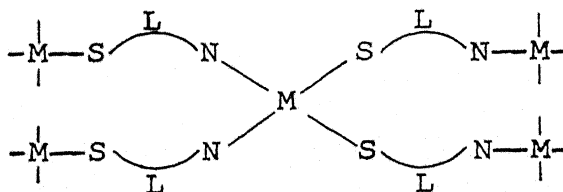
M may be additionally bonded to bases as given in Tables II.1 and II.2.

Table II.1. Metal Complexes of Co(II) and Ni(II) Ions

Compound	Colour	Analyses: Found (Calcd.), %					μ_{eff}* (B.M.)
		M	S	C	H	N	
1	2	3	4	5	6	7	8
$Co(MPQ)_2(py)H_2O$	Dirty green	9.1 (8.9)	10.0 (9.7)	59.6 (59.8)	3.8 (3.7)	10.7 (10.6)	4.95
$Co(MPQ)_2(\beta-pic)_2$	Light green	8.0 (7.9)	8.7 (8.5)	63.7 (63.9)	4.1 (4.3)	11.0 (11.2)	4.82
$Co(MPQ)_2(imzH)H_2O$	Steel grey	9.0 (9.1)	9.9 (9.8)	57.0 (57.1)	3.9 (3.7)	13.1 (12.9)	4.90
$Co(MPQ)_2(o-phen)$	Orange yellow	8.1 (7.9)	8.7 (8.6)	64.2 (64.4)	3.4 (3.5)	11.5 (11.3)	4.70
$Co(MPQ)_2(bipy)$	Greenish brown	8.3 (8.2)	8.7 (8.9)	63.4 (63.2)	3.5 (3.6)	11.6 (11.7)	4.75
$Co(MPQ)_2(pzH)$	Orangish pink	9.1 (9.3)	10.3 (10.1)	58.9 (58.7)	3.3 (3.5)	13.1 (13.3)	4.25
$Ni(MPQ)_2$	Light grey	10.3 (10.4)	11.5 (11.3)	59.6 (59.5)	3.1 (3.2)	9.7 (9.9)	3.74
$Ni(MPQ)_2(py)_2$	Green	8.4 (8.2)	8.8 (8.9)	63.2 (63.1)	3.8 (3.9)	11.4 (11.6)	3.17

Table II.1 (contd.)

1	2	3	4	5	6	7	8
$Ni(MPQ)_2(\beta\text{-pic})_2$	Light green	8.1 (7.9)	8.3 (8.5)	63.7 (63.9)	4.1 (4.3)	11.3 (11.2)	3.07
$Ni(MPQ)_2(imzH)H_2O$	Greenish brown	9.3 (9.1)	9.6 (8.9)	57.2 (57.1)	3.8 (3.7)	13.0 (12.9)	3.18
$Ni(MPQ)_2(o\text{-phen})$	Light grey	8.0 (7.9)	8.7 (8.6)	64.6 (64.4)	3.4 (3.5)	11.2 (11.3)	3.02
$Ni(MPQ)_2(bipy)$	Yellowish green	8.1 (8.2)	9.0 (8.9)	63.1 (63.2)	3.6 (3.6)	11.8 (11.7)	3.14

*At $20^{o}C$ and uncorrected for diamagnetism.

Table II.2. Analytical Data of Complexes

Compound	Colour	m.p. (°C)	Analyses: Found (Calcd.), %					
			M	S	C	H	N	Cl
1	2	3	4	5	6	7	8	9
[Pd(MPQ)$_2$]	Orange	270*	17.6 (17.4)	10.6 (10.5)	55.1 (54.9)	3.1 (2.9)	9.3 (9.1)	–
[Pd(MPQ)Cl(Py)]	Orange	210d	22.2 (22.5)	6.9 (6.8)	47.8 (48.1)	2.7 (3.0)	9.0 (8.9)	7.7 (7.5)
[Pd(MPQ)Cl(β-pic)]	Brown yellow	278	21.6 (21.8)	6.4 (6.6)	49.5 (49.2)	3.4 (3.3)	8.9 (8.6)	7.6 (7.3)
[Pd(MPQ)Cl(o-phen)$_{1/2}$]	Orange yellow	270d	22.1 (21.9)	6.8 (6.6)	49.3 (49.5)	2.8 (2.7)	8.4 (8.7)	7.0 (7.3)
[Pd(MPQ)Cl(bipy)$_{1/2}$]	Yellow	280d	22.7 (22.5)	6.5 (6.8)	48.0 (48.2)	2.6 (2.7)	9.1 (8.9)	7.7 (7.5)
[PdCl(MPQH)(imz)]	Yellow	275d	23.2 (23.0)	7.2 (6.9)	43.8 (44.1)	2.9 (2.8)	9.3 (9.1)	7.4 (7.7)
[Pt(MPQ)$_2$]	Light yellow	260*	27.6 (27.8)	9.0 (9.1)	48.2 (47.9)	2.7 (2.6)	8.2 (8.0)	–
[Pt(MPQ)$_2$(Py)]	Yellow	290*	24.8 (25.0)	8.4 (8.2)	51.0 (50.8)	3.1 (3.0)	9.2 (9.0)	–

Table II.2 (contd.)

1	2	3	4	5	6	7	8	9
$[Pt(MPQ)_2(\beta\text{-pic})]$	Light yellow	273d	24.4 (24.6)	8.2 (8.1)	51.7 (51.4)	3.0 (3.2)	8.6 (8.8)	—
$[Pt(MPQ)_2(o\text{-phen})_{1/2}]$	Grey	268d	24.4 (24.7)	8.3 (8.1)	51.3 (51.6)	3.0 (2.8)	9.0 (8.9)	—
$[Pt(MPQ)_2(bipy)_{1/2}]$	Light brown	250d	24.9 (25.0)	8.4 (8.2)	51.1 (50.8)	2.6 (2.8)	9.3 (9.0)	—
$[Pt(MPQ)_2(imz)Cl]$	Greenish brown	290d	24.0 (24.3)	8.2 (8.0)	46.1 (46.3)	2.4 (2.6)	10.4 (10.5)	4.6 (4.4)
$[Pt(MPQ)_2(pz)Cl]$	Steel grey	265d	24.0 (24.3)	8.2 (8.0)	46.0 (46.4)	2.4 (2.6)	10.2 (10.5)	4.7 (4.4)
$[Pt(MPQ)_2(pyrm)_{1/2}]$	Greenish brown	268	26.0 (26.3)	8.9 (8.6)	48.4 (48.6)	2.5 (2.7)	9.7 (9.4)	—

Py = pyridine; β-pic = β-picoline; o-phen = orthophenanthroline; imzH = imidazole;
pzH = pyrazole; pyrm = pyrimidine; * = no change upto.

Table II.3. Major IR Bands of Interest (in cm^{-1})

| Compound | $\nu(NH)$ | $\nu(H_2O)$ | $\nu(CO)$ | Thioamide Bands | | | |
				I	II	III	IV
Ligand (MPQH)	3250m	–	1660s	1540s	1345s	1000m	770s
Co(MPQ)$_2$(py)H$_2$O	–	3400br	1665s	1485s	1285s	1000m	750s
Co(MPQ)$_2$(β-pic)$_2$	–	–	1660s	1475s	1280s	1005m	760s, 780s
Co(MPQ)$_2$(imzH)H$_2$O	–	3300-3350br	1660s	1485s	1285s	1005m	750s
Co(MPQ)$_2$(o-phen)	–	–	1660s	1470m	1280m	1000w	740s
Co(MPQ)$_2$(bipy)	–	–	1660s	1470m	1280m	1000w	740s, 750s
Co(MPQ)$_2$(pzH)	3580s	–	1710s	1530m	1350w) 1320w)	1000w	760s
Ni(MPQ)$_2$	–	–	1650s	1525s	1330s	1000m	760s
Ni(MPQ)$_2$(py)$_2$	–	–	1660s	1480s	1280m	1005w	740s
Ni(MPQ)$_2$(β-pic)$_2$	–	–	1665s	1480m	1280m	1010w	760m
Ni(MPQ)$_2$(imzH)H$_2$O	–	3500br	1660s	1480s	1280m	1010m	740s, 750s
Ni(MPQ)$_2$(o-phen)	–	–	1660s	1480s	1285m	1010w	745s
Ni(MPQ)$_2$(bipy)	–	–	1660s	1480s	1280m	1010m	740s, 750s

s = strong; m = medium; w = weak; br = broad.

Table II.4. Thioamide IR Bands of the Ligand and Complexes
          (cm^{-1})

Complex	ν(NH)	ν(C=O)	Thioamide Bands			
			I	II	III	IV
Ligand (MPQH)	3250m	1660s	1540s	1345	1000s 980m	770s
$[Pd(MPQ)_2]$	–	1690s	1510s	1320s 1340s	990s	755s
$[Pd(MPQ)Cl(py)]$	–	1715m	1535m	1230m	1005m	770s
$[Pd(MPQ)Cl(\beta-pic)]$	–	1700s	1520s	1325s 1350s	990s	760s
$[Pd(MPQ)Cl(o-phen)_{1/2}]$	–	1710s	1530s	1335m 1360m	1000m	750m 770s
$[Pd(MPQ)Cl(bipy)_{1/2}]$	–	1700s	1540m 1560m	1330m 1355m	1000m	770m
$[PdCl(MPQH)(imz)]$	3240m) 3260m) br	1700s	1530s 1550s	1330s 1350s	990s	760s
$[Pt(MPQ)_2]$	–	1690s	1510s	1325s 1365s	990s	760s
$[Pt(MPQ)_2(py)]$	–	1680s	1525s	1300m 1340m	975s 1010w	765s 775s
$[Pt(MPQ)_2(\beta-pic)]$	–	1700s	1530m 1560m	1340m 1365m	980m	770s 780s 790s
$[Pt(MPQ)_2(o-phen)_{1/2}]$	–	1700s	1530m 1560m	1340m 1365m	975s	770s 780s
$[Pt(MPQ)_2(bipy)_{1/2}]$	–	1705s	1530m 1560m	1335m 1365m	975s 1000w	770s
$[Pt(MPQ)_2(imz)Cl]$	–	1700s	1560s	1340m 1360m	975m	770s 780s
$[Pt(MPQ)_2(pz)Cl]$	–	1700s	1560m	1340m 1360m	975s	770s 780s
$[Pt(MPQ)_2(pyrm)_{1/2}]$	–	1690s	1520m 1550m	1330m 1355m	970m 990m	760s

Table II.5. The Solid Reflectance Spectra of Some of Represen-
            tative Co(II) and Ni(II) Complexes and Their Assign-
            ments

Compound	λ_{max} (nm)	Assignment
$[\text{Co(MPQ)}_2(\text{py})\text{H}_2\text{O}]$	250	IL
	310br	IL
	485w	$\nu_3 \ [^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)]$
	610vw	$\nu_2 \ [^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)]$
$[\text{Co(MPQ)}_2(\beta\text{-pic})_2]$	250	IL
	310br	IL
	395sh	CT
$[\text{Co(MPQ)}_2(\text{imzH})\text{H}_2\text{O}]$	250	IL
	310	IL
	500w	$\nu_3 \ [^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)]$
	595w,br	$\nu_2 \ [^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)]$
$[\text{Co(MPQ)}_2(\text{o-phen})]$	250	IL
	300w,br	IL
	394w,br	CT
	525) w,sh 555)	$\nu_3 \ [^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)]$
$[\text{Ni(MPQ)}_2]$	310w,br	IL
	376sh	CT
	680w,br,sh	$\nu_3 \ [^3T_1(F) \longrightarrow {}^3T_1(P)]$
$[\text{Ni(MPQ)}_2(\text{py})_2]$	250	IL
	364w,br,sh	CT
	395w,sh	$\nu_3 \ [^3A_{2g}(t) \longrightarrow {}^3T_{1g}(P)]$
	625br,sh	$\nu_2 \ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)]$

Table II.5 (contd.)

Compound	λ_{max} (nm)	Assignment
$[Ni(MPC)_2(\beta\text{-pic})_2]$	250	IL
	334br,sh	CT
	610w,br,sh	$\nu_2\ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)]$
$[Ni(MPC)_2(imzH)H_2O]$	280	IL
	376sh	CT
	430br,sh	$\nu_3\ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)]$
$[Ni(MPC)_2(o\text{-phen})$	250	IL
	304w,br	IL
	475sh	$\nu_3\ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)]$
	568w,br	$\nu_2\ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)]$
$[Ni(MPC)_2(bipy)]$	250	IL
	325w,sh	IL or CT
	460br,sh	$\nu_3\ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)]$
	590br	$\nu_2\ [^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)]$

vw = very weak; sh = shoulder; br = broad.

Table II.6. Reflectance Spectra of the Complexes

Compound	Band position λ_{max} (nm)	Assignment	Δ_1 (cm^{-1})
1	2	3	4
[Pd(MPQ)$_2$](in DMF)	292sh	IL	
	335sh	CT	
[Pd(MPQ)Cl(py)]	700–420	CA	
	410w,sh	$^1A_{1g} \longrightarrow {}^1B_{1g}$	26490
	345br	CT	
	295sh	IL	
[Pd(MPQ)Cl(β-pic)]	700–420	CA	
	410w,sh	$^1A_{1g} \longrightarrow {}^1B_{1g}$	26490
	355sh	CT	
	285w,br	IL	
[Pd(MPQ)Cl(o-phen)$_{1/2}$]	700–360	CA	
	340br	CT	
[Pd(MPQ)Cl(bipy)$_{1/2}$]	700–460	CA	
	430sh	$^1A_{1g} \longrightarrow {}^1B_{1g}$	25356
	320br	CT	
[PdCl(MPQH)(imz)]	700–500	CA	
	440sh	$^1A_{1g} \longrightarrow {}^1B_{1g}$	24827
	340sh	CT	
[Pt(MPQ)$_2$(β-pic)]	700–380	CA	
	375w,sh	d–d	28766
	335w,sh	CT	
	290w,sh	IL	
[Pt(MPQ)$_2$(o-phen)$_{1/2}$]	700–350	CA	
	370sh	d–d	28857
	335w,sh	CT	
	295w,sh	IL	
	265w,sh	IL	

Table II.6. (contd.)

1	2	3	4
$[Pt(MPQ)_2(bipy)_{1/2}]$	700–360	CA	
	370w,sh	d–d	28857
	300sh	IL	
$[Pt(MPQ)_2(imz)Cl]$	700–360	CA	
	340w,sh	CT	
$[Pt(MPQ)_2(pz)Cl$	700–360	CA	
	340w,sh	CT	
	295w,sh	IL	

CA = Continuous absorption

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Fig.II.1 IR Spectra

① MPQH
② [Co(MPQ)₂(pzH)]

③ [Co (MPQ)$_2$ (py) H$_2$O]

④ [Ni (MPQ)$_2$ (β – pic)$_2$]

Fig.II.1 IR Spectra

Wavenumber (cm^{-1})

⑤ [Pd(MPQ)$_2$]
⑥ [Pt(MPQ)$_2$(pz)Cl]

Fig.II.1 IR Spectra

Wavenumber (cm^{-1})
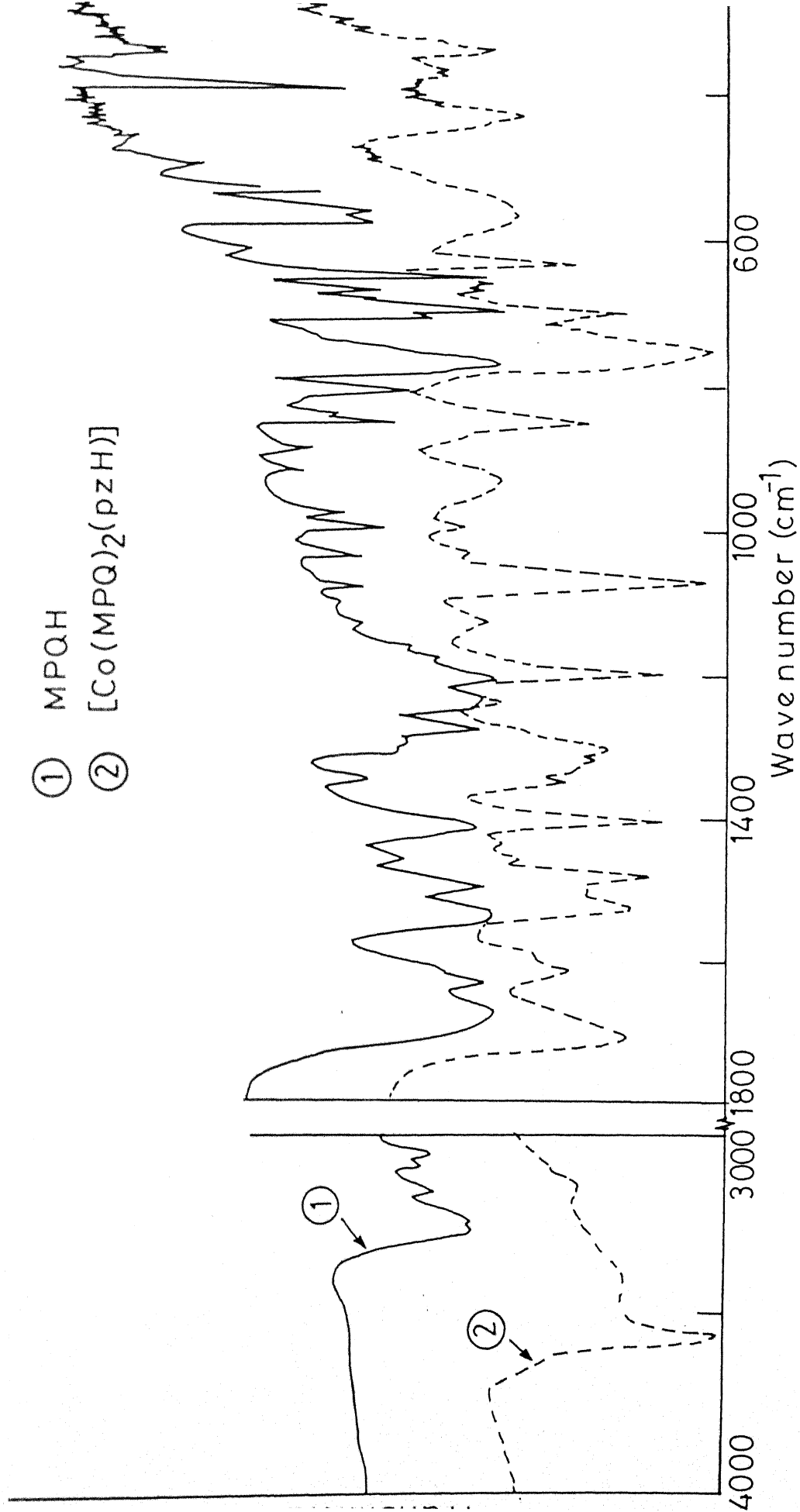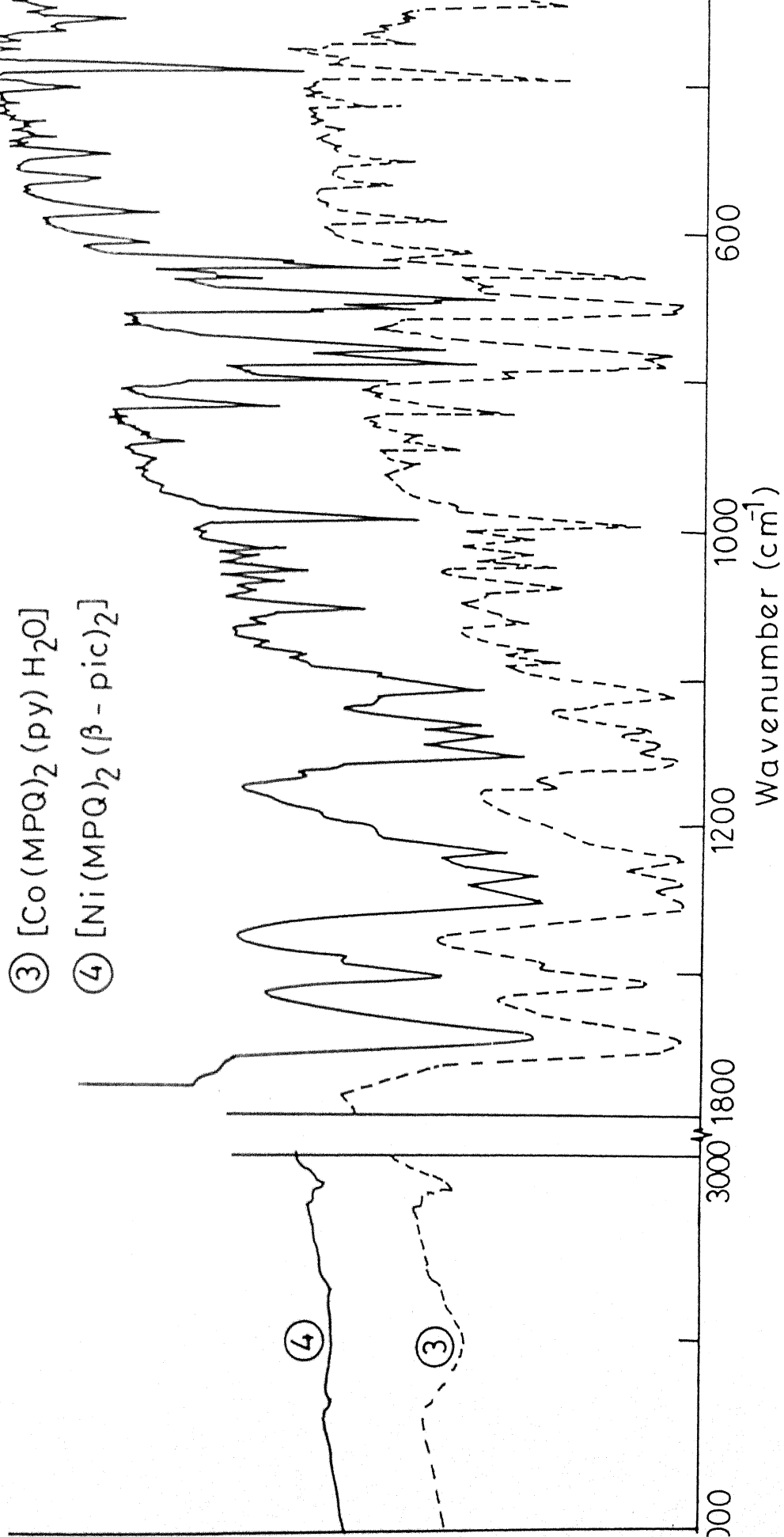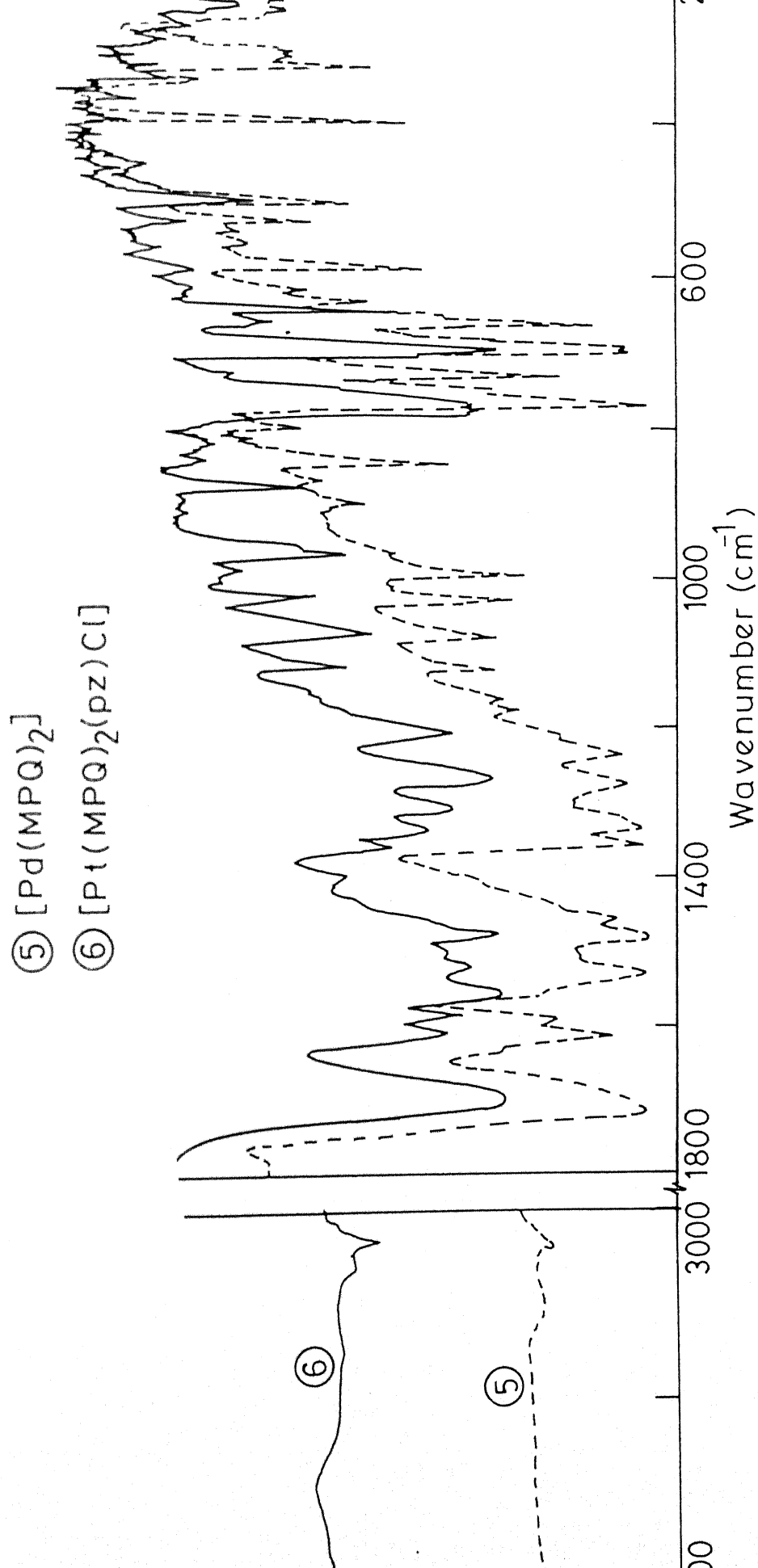
Chapter III

SYNTHESES AND CHARACTERISATION OF RUTHENIUM(III),
RHODIUM(III) AND NOVEL OXOMANGANESE COMPLEXES OF
2-MERCAPTO-3-PHENYL-4-QUINAZOLINONE: ESR STUDIES
ON d^5 SYSTEMS

This chapter describes the reactions of the ligand (MPQH)
with $MnCl_2.4H_2O$, $RuCl_3.3H_2O$ and $RhCl_3.3H_2O$ in basic medium in
the presence and absence of various N-heterocyclic bases. An
ankaline alcoholic solution of MPQH reacts with $MnCl_2.4H_2O$ and
leads to the formation of oxo-manganese adduct MnO(MPQH) and
when this reaction is carried out in the presence of N-hetero-
cyclic bases, the compounds obtained were $MnO(MPQH)_2B$ (B = py,
β-pic, o-phen) and $MnO(H_2O)(MPQH)_{1/2}$ (bipy). The reactions of
MPQH with $RuCl_3.3H_2O$ and $RhCl_3.3H_2O$ afford the compounds $Ru(MPQ)_2$-
$Cl.2H_2O$, $Rh(MPQ)(MPQH)Cl_2.2H_2O$ and $Ru(MPQ)_2Cl.DMF$ (in dimethyl-
formamide medium). The reactions of $RuCl_3.3H_2O$ with MPQH in the
presence of bases lead to the formation of complexes of the type

$Ru(MPQ)_2Cl.B(H_2O)$ (B = py, β-pic, imzH) and $Ru(MPQ)Cl_2(o-phen)-H_2O$. These complexes were characterised on the basis of analytical, spectral (ir, uv-visible), magnetic, conductivity and ESR studies. Their tentative structures have been proposed.

III.1 EXPERIMENTAL

All the chemicals used were of AnalaR or chemically pure grade. The ligand MPQH was prepared as described in Chapter II. The methods of analyses, recording of ir, uv and visible spectra, measurements of magnetic susceptibilities and melting points have been described in Chapter II. The ESR spectra were recorded on 109E-line Century Series EPR spectrometer at X-band frequencies at 293 K using DPPH (g = 2.0036) as internal standard. Ruthenium was estimated on a IL-751 atomic absorption spectrophotometer after the weighed amount (8-12 mg) of the complex was decomposed by heating with mixture of H_2SO_4 and HNO_3 upto almost dryness several times until the resulting residue gave a clear solution when taken in about 20 ml of water. It was filtered and diluted with distilled water to a volume of 50 ml. As the sensitivity of the instrument for ruthenium metal is from 0.8 μg/ml to 50 μg/ml, the five standard solutions were prepared of the concentration of 10, 20, 30, 40 and 50 μg/ml. The 0.0513 g of $RuCl_3.3H_2O$ was dissolved in 20 ml 1:1 HCl and diluted with distilled water to a volume of 500 ml to give a solution of the concentration of 50 μg/ml of ruthenium. From this solution, the other standard solutions were prepared by appropriate dilution

The concentration of sample solution must lie in the range of standard solutions.

Preparation of the Complexes

(1) <u>General method of preparation of the oxo-manganese(II) adducts MnO(MPQH); MnO(MPQH)B(B = py, β-pic or o-phen) and MnO(MPQH)$_{1/2}$(bipy)</u>

To a 25 ml aqueous solution of $MnCl_2.4H_2O$ (0.4 g, ≃ 2 mmol) containing heterocyclic bases*, a 50 ml alkaline ethanolic solution of ligand** (1.02 g, ⌣ 4 mmol) was added with stirring followed by refluxing for an hour. The resultant precipitates were separated by filtration through sintered crucible, washed several times with water, ethanol and ether and dried <u>in vacuo</u>.

(2) <u>Chlorobis(2-mercapto-3-phenyl-4-quinazolinato)dimethylformamide ruthenium(III), [Ru(MPQ)$_2$Cl.DMF]</u>

Solution of $RuCl_3.3H_2O$ (0.26 g, 1 mmol) in 10 ml of DMF was added to a filtered solution of MPQH (0.5 g) in 25 ml of DMF. The resulting solution was refluxed for an hour. The

---

* 5 ml of pyridine, β-picoline; 15 ml ethanolic solution of 1,10-phenanthroline (0.4 g, ⌣ 2 mmol); 15 ml of ethanolic solution of 2,2'-bipyridine (0.312 g, ⌣ 2 mmol). No base is required in case of MnO(MPQH).

** 0.5 g of MPQH was taken in case of MnO(MPQH) and 0.254 g of MPQH was taken for the preparation of MnO(MPQH)$_{1/2}$(bipy).

solution was concentrated to about 5 ml on water bath, on cooling violet precipitate resulted which was filtered, washed with alcohol and ether and dried at $80^{\circ}C$.

(3) Rh(MPQ)(MPQH)Cl$_2$.2H$_2$O

Solution of RhCl$_3$.3H$_2$O (0.26 g, 1 mmol) in 10 ml of DMF was added to filtered solution of MPQH (0.508 g, 2 mmol in 25 ml of DMF. The resulting solution was heated under reflux with constant stirring for an hour. The solution was allowed to cool at room temperature. Addition of excess ammonia solution to it precipitated a yellow complex which was centrifuged, washed with water, alcohol and ether and dried at $80^{\circ}C$.

(4) General method of preparation of Ru(MPQ)$_2$Cl.B.H$_2$O (B = H$_2$O, py, β-pic or imzH) and Ru(MPQ)Cl$_2$(o-phen)H$_2$O

A filtered alkaline (pH = 9-10) ethanolic solution (25 ml) of MPQH (0.5 g, 2 mmol)* was added to an aqueous solution (50 ml) RuCl$_3$.3H$_2$O (0.26 g, 1 mmol) containing appropriate base solution.** The resulting solution was heated under reflux for 15 hrs. The resultant precipitates were filtered, washed thoroughly with water, a little amount of alcohol and ether. The compounds were recrystallised from methanol.

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* 0.25 g of MPQH in case of Ru(MPQ)Cl$_2$(o-phen)H$_2$O

** 5 ml of pyridine, β-picoline, 5 ml alcoholic solution of 1,10-phenanthroline (0.2 g, 1 mmol) or 5 ml aqueous solution of imidazole (0.07 g, 1 mmol).

III.2 RESULTS AND DISCUSSION

Analytical data are consistent with the stoichiometry proposed for complexes (Tables III.1 and III.2). All oxo-manganese compounds are insoluble in water and common organic solvents and probably are polymeric in nature. Ruthenium and rhodium compounds are non-conducting.

III.2.1 IR Spectra (Tables III.3 and III.4)

III.2.1.1 Oxo-manganese compounds

ν(NH) of ligand (MPQH) broadens considerably after complexation indicating the possible coordination through nitrogen of N-H group. The ν(CO) of the MPQH shifts towards higher wave number by 10-20 cm^{-1} in the spectra of the complexes, ruling out the involvement of C=O group in metal bonding. The thioamide band I which has principal contributions from $(\delta_{N-H} + \delta_{C-H})$ remains almost stationary but intensity of the band is reduced after complexation indicating that the MPQH is coordinated through nitrogen without deprotonation. The band II $(\nu_{C=S} + \nu_{C-N} + \delta_{C-H})$ shifts ± 10 cm^{-1} after complexation and its intensity reduces to such an extent that in some cases, this band almost disappeared, suggesting the simultaneous coordination through N and S. The thioamide band III $(\nu_{C \cdots N} + \nu_{C \cdots S})$ is of very low intensity in the ir spectra of the complexes. The thioamide band IV $(\nu C \cdots S)$ does not considerably change after complexation. Red shift of 25-55 cm^{-1} for the thioamide IV band indicates coordination through sulphur whereas bonding

through nitrogen causes a blue shift of 40-90 cm^{-1} for this band. Simultaneous coordination through nitrogen and sulphur both does not produce appreciable shift in the position of the thioamide IV band. A broad band at 3400-3500 cm^{-1} in the compound $MnO(H_2O)(MPQH)_{1/2}$(bipy) is assigned to ν(OH). Although it is difficult to rule out the possibility of two -OH groups in this complex on the basis of IR data only, but since all compounds synthesized using similar method of preparation and other compounds do not show any band in this region hence attribution of this band to ν(OH) of water is more logical. The bands of medium intensity at around 650($\pm$5) and 845($\pm$5) cm^{-1} in the spectra of the complexes is assigned to ν(Mn-O) and ν(Mn=O), respectively[1] but until ^{18}C isotopic labelling is carried out, any such assignment in such a complex system will be tentative. New bands of weak to medium intensity in the region 250-400 cm^{-1} may be due to coupled vibrations of ν(Mn-N) and ν(Mn-S). There seems to be extensive mixing between the bands of the ligand and those of N-heterocyclic bases, hence characteristic frequencies did not occur at their standard positions.

III.2.1.2   Ru(III) and Rh(III) complexes

The disappearance of ν(NH) band of the MPQH at 3250 cm^{-1} from spectra of all the complexes except $Rh(MPQ)(MPQH)Cl_2 \cdot 2H_2O$ indicates the displacement of N-H hydrogen by metal ion and formation of metal-nitrogen bond. The presence of weak broad band at 3240-60 cm^{-1} in the ir spectrum of Rh(III) complex indicates

that one ligand is coordinated as MPQH. The weakening and broaden ning of ν(NH) after complexation can be tentatively assigned to Rh(III)-N bond formation. The presence of broad band in the spectra of $[Ru(MPQ)_2Cl(imzH)].H_2O$ may be assigned as mixed band of ν(NH) of imidazole and γ(OH) of water. The γ(C=O) band of the ligand at 1660 cm^{-1} shifts towards higher wavenumber by 10 to 30 cm^{-1} in the spectra of the complexes, indicating the noninvol-vement of C=O group in metal bonding. The ν(C=O) of DMF in $[Ru(MPQ)_2Cl.DMF]$ is probably merged with the band present at 1690 cm^{-1} in the ir spectrum of the complex. The ν(C=O) in DMF appears[2] at 1683 cm^{-1} hence coordination of DMF through its N-atom is likely. The thioamide band I of the ligand at 1540 cm^{-1} shifts to lower wavenumber by 20-35 cm^{-1} in the spectra of the complexes. This indicates the M-N bond formation as the thioamide band I has principal contribution from $(\delta_{C-H} + \delta_{N-H})$. The band II of the ligand at 1345 cm^{-1} either splits or shifts to lower wavenumber as a result of coordination. The band III is relatively weak in the spectra of the complexes. The thio-amide band IV of the ligand at 770 cm^{-1} changes its position by $\pm$10 cm^{-1}. This small shift of the band IV may be attributed to simultaneous coordination through nitrogen and sulfur. New bands of weak to medium intensity in the region 250-500 cm^{-1} in the spectra of the complexes may be assigned to coupled vibrations ν(M-Cl), ν(M-N) and ν(M-S).[3] In the spectra of the complexes, the characteristic frequencies of N-heterocycles did not occur at their standard positions as the result of

mixing of bands of MPQH and those of bases.

III.2.2 Electronic Spectra

III.2.2.1 Oxo-manganese complexes

Owing to insolubility of the complexes, their electronic spectra were recorded in solid state. The band positions and assignments are listed in Table III.5.

The reflectance spectra of these complexes exhibit almost continuous absorption in the region 700-300 nm. The weak forbidden d-d transitions for high spin manganese(II) are probably masked by this continuous absorption or strong charge transfer (CT) transitions. However, the weak shoulders around 350 nm, 460 nm and 470 nm in some of the complexes may be assigned to charge transfer (CT) transitions, $^6A_{1g}(^6S) \rightarrow {}^4T_{2g}(^4G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{1g}(^4G)$, respectively.[4] A shoulder at 285-300 nm may be assigned to intraligand (IL) transition as the electronic spectrum of MPQH in DMF exhibits one strong transition at 295 nm and one weak shoulder at 262 nm which are assigned to $\pi \rightarrow \pi*$ intraligand (IL) transition.

III.2.2.2 Ru(III) and Rh(III) complexes

Electronic spectra of Ru(III) and Rh(III) complexes were taken in methanol solution (Table III.6).

The ground state of Rh(III), d^6 system, is $^1A_{1g}$. The ligand field transition[5] $t_{2g}^6 \rightarrow t_{2g}^5 e_g'$ gives $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$

and $^1T_{2g}$ as the excited states in the increasing order of their energies. According four bands can be expected corresponding to $^1A_{1g} \rightarrow {}^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$, respectively. The spin forbidden transitions $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^3T_{2g}$ are, generally not observed. Bands corresponding to charge transfer from ligand to metal generally do not appear in the visible region in case of low spin d^6 systems. The electronic spectrum of Rh(MPQ)(MPQH)-$Cl_2.2H_2O$ shows only intraligand transitions. The other expected d-d transitions were probably masked by continuous absorption in visible region or IL bands.

The ruthenium(III) complexes showed the bands in the region 645-655, 525-565 and 415-465 nm (Table III.3) which may be assigned to $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$ transitions, respectively.[6,7] Some of these transitions could not be observed in some of spectra of Ru(III) complexes. A broad or shoulder around 295-310 nm is assigned to intraligand transition. Another band at 330 nm in the spectrum of $[Ru(MPQ)_2Cl(Py)].H_2O$ may be assigned to M $\rightarrow$ L or L $\rightarrow$ M charge transfer (CT) transition.

III.2.3 Magnetic Susceptibilities of the Complexes (Tables III.1 and III.2)

III.2.3.1 Oxo-manganese(II) Complexes

Magnetic susceptibilities, hence magnetic moments, at room temperature were found in the range of 5.7 - 6.1 B.M. for all Mn(II) complexes except MnO(MPQH) and these are in good agreement

with high spin octahedral Mn(II) complexes. The magnetic moment
of MnO(MPQH) was found to be 4.24 B.M. which is consistent with
square planar geometry around d^5 Mn(II) ions.

III.2.3.2 Ru(III) and Rh(III) Complexes

Rh(MPQ)(MPQH)Cl$_2$.2H$_2$O was found to be diamagnetic and the
magnetic moments of all Ru(III) complexes lie in the range 1·7 to
2.1 B.M. corresponding to one unpaired electron.

III.2.4 ESR Spectra

III.2.4.1 Mn(II) Complexes

The spin Hamiltonian usually used to fit the spectra of
high spin d^5 systems, notably in system containing Fe^{3+} or
Mn^{2+}, is

$$\mathcal{H} = \beta H \cdot g \cdot S + D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2), \qquad \ldots (1)$$

originally proposed by Bleaney and Stevens.[8] Some authors also
include quartic terms but these are usually small and are justi-
fiably omitted here. The terms D and E (D and E are measures
of axial distortion and rhombic distortion, respectively) are
thought to arise for a variety of reasons, the most important
involving the first order matrix elements of axial and rhombic
fields between excited quartet states, and the matrix elements
for spin-orbit coupling between these states and the ground
state. It is to be noted that the excited quartet states must

first have been admixed into one another by the cubic component of crystalline field[9] but that their effect on the ground state does not necessarily reflect the symmetry of the field[10] as is usually supposed. If D and E are zero then a isotropic absorption line with a g value slightly greater than 2 is usually observed,[11] but it is not always true as some of manganese compounds studied give single resonance like g_{eff} = 2, eventhough it is clear that the structure can not be regular and an appreciable zero field is expected.[12] If D and E are finite but small (0.001-0.1 cm^{-1}) five ESR transitions are observed and are well understood.[13] In the event that D or E is large compared of g.β.H, for the two limiting cases D $\neq$ 0, E = 0 and D = 0, E $\neq$ 0, the eigenvalues and eigenvectors of (1) in zero magnetic field are easily found to be three kramers doublets. In the first case the lowest doublet has the effective[14] g values $g_{||}$ = 2, $g_{\perp}$ = 6 and is exemplified experimentally in strong axially symmetric electric fields, e.g., in myglobin derivatives[15] and in Fe^{3+} impurities in strontium titanate.[16] In the second case the middle doublet has an isotropic effective g value of 4.29. Castner et al.[17] were the first to propose (D=0, E$\neq$0) to account for the g = 4.27 spectrum found for ferric ion in glass. ESR signals close to 4 often occur in biological materials and have been accounted for in the same way.[18,19] Griffith defended this original interpretation of the g = 4.29 signal but showed that so long as the environment of the d^5 ion is more symmetric than the overall symmetry group of the site in a special way, then D need not be

zero but shall be small. The special environments are tetra-
hedral MA_2B_2 (C_{2v}), distorted octahedral MA_6 (D_{2h}) and octa-
hedral MA_3B_3 (C_{2v}), in all of which the excited $^4T_1$ state is
split into three equally spaced components. Castner et al.
consider that a small D term would have the effect of broaden-
ing the line at g = 4.29. Wickman et al. calculated the ratio
of E/D(= λ) from the observation of such a broadening in the
spectrum of ferrichrome A.[20]

In the event that both D and E are large compared with
g·β·H, various authors[20-22] have shown that the g = 4.29 signal
can rise if λ, the ratio of E to D, is 1/3. It might be
thought this situation could arise accidentally in a few
instances, but this could hardly be the correct interpretation
for such a widespread phenomenon. However, it was elegantly
pointed out by Blumberg[23] that if λ = 0 represents axial symme-
try (D$\neq$0, E=0), then an increase in λ represents a departure
towards rhombic symmetry. λ = 1/3 represents maximum possible
rhombic symmetry with equally spaced Kramers doublets and values
of λ greater than 1/3 represents a conversence towards axial
symmetry again, with λ = 1 representing entirely axial symmetry;
thus ESR signals near g = 4.29 are expected if λ is near 1/3.
But it is to be noted[10] that equally spaced energy levels do
not necessarily imply complete rhombic symmetry.

R.D. Dowsing and J.F. Gibson[24] have determined by nume-
rical computation eigenvalues and eigenfunctions of the Hamil-
tonian, Equation (1), excluding the quartic terms, but including

$g\beta H$, thus avoided any undesirable assumptions about the size of D and E relative to $g\beta H$ which were inherent in the perturbation treatments. Also, using the eigenfunctions thus determined computed transition probabilities within and between the three Kramers doublets, thus predicted, for a given microwave frequency, where ESR lines are to be expected for various values of D and λ. Finally they made the plots which show the probability of an ESR transitions as a function of axial distortion, D, versus magnetic field, H, with λ parameter (E/D) being held constant. It is simple to use the D versus H graphs at different λ values to select the best fit of D and λ for a given ESR spectrum, particularly if transitions other than the middle doublet g = 4.29 transition or the lower doublet $g_{||}$ = 2.0, $g_{\perp}$ = 6.0 transition, are observed. R.D. Dowsing and J.F. Gibson pointed out the following salient features for X-band spectra. (1) For D >0.1 cm^{-1}, an absorption, if λ is close to $\frac{1}{3}$, is expected between 650-700 Gauss. The intensity of this transition is always expected to weak. (2) A line at fields lower than 650 G is necessarily a normal "allowed" transition from which it follows that the zero fields splitting between a pair of Kramers doublets is of order of $h\nu$. (3) The absorption at about 1500 G is expected if $\lambda \simeq \frac{1}{3}$ and D >0.23 cm^{-1}. This line broadens or splits as λ departs from $\frac{1}{3}$. (4) The observation of several lines at fields between 5000 & 15000 G means that D lies between 0.1 and 0.6 cm^{-1}. (5) For nearly axial symmetry (λ close to zero), observation of $g_{||}$ band at about 1100 G and the $g_{\perp}$ band at 3300 G means that D $\geqslant 0.2$ cm^{-1}. (6) For

axial symmetry a strong single band at 1100 G indicates that $\lambda = 0$. This band will split or will broaden as λ increases, and may still be discerned at $\lambda = 0.1$. This bands moves up in field as D decreases below 0.2 cm^{-1}.

The estimation of D and λ values for Mn(II) compounds reported here was made by comparing the data (Table III.7) obtained from observed ESR spectra with aforesaid electron spin resonance probability plots.[24-26]

MnO(MPQH)$_2$(o-phen) and MnO(H$_2$O)(MPQH)$_{1/2}$(bipy) show strong transitions at the field 3300 (g_{eff} = 2.00) and 3288 (g_{eff} = 2.01) Gauss, respectively along with some other broad transitions. As strong absorption is an indication of geometry of the compound these transitions ($g_{eff} \simeq 2.00$) are typical of nearly axial symmetry (λ close to zero) with tetragonal distortion, D, greater than 0.02 cm^{-1}. Thus both compounds MnO(MPQH)$_2$-(o-phen) and MnO(H$_2$O)(MPQH)$_{1/2}$(bipy) have low λ values in the range 0.00 - 0.01 cm^{-1} and from the comparison of remaining line(s) of spectra of these two compounds with ESR transition probability plots (Fig.III.a & b) the axial distortion, D, could be assigned as 0.095 and 0.12 cm^{-1}, respectively. These assignments are somewhat similar with those of the high spin Mn(II) complexes reported by Potter and Taylor.[27]

The spectra of MnO(MPQH)$_2$(py) and MnO(MPQH)$_2$(β-pic) show a single broad (250 G linewidth) absorption at 3300 G with g_{eff} value of 2.00. As these compounds are polymeric in nature. It
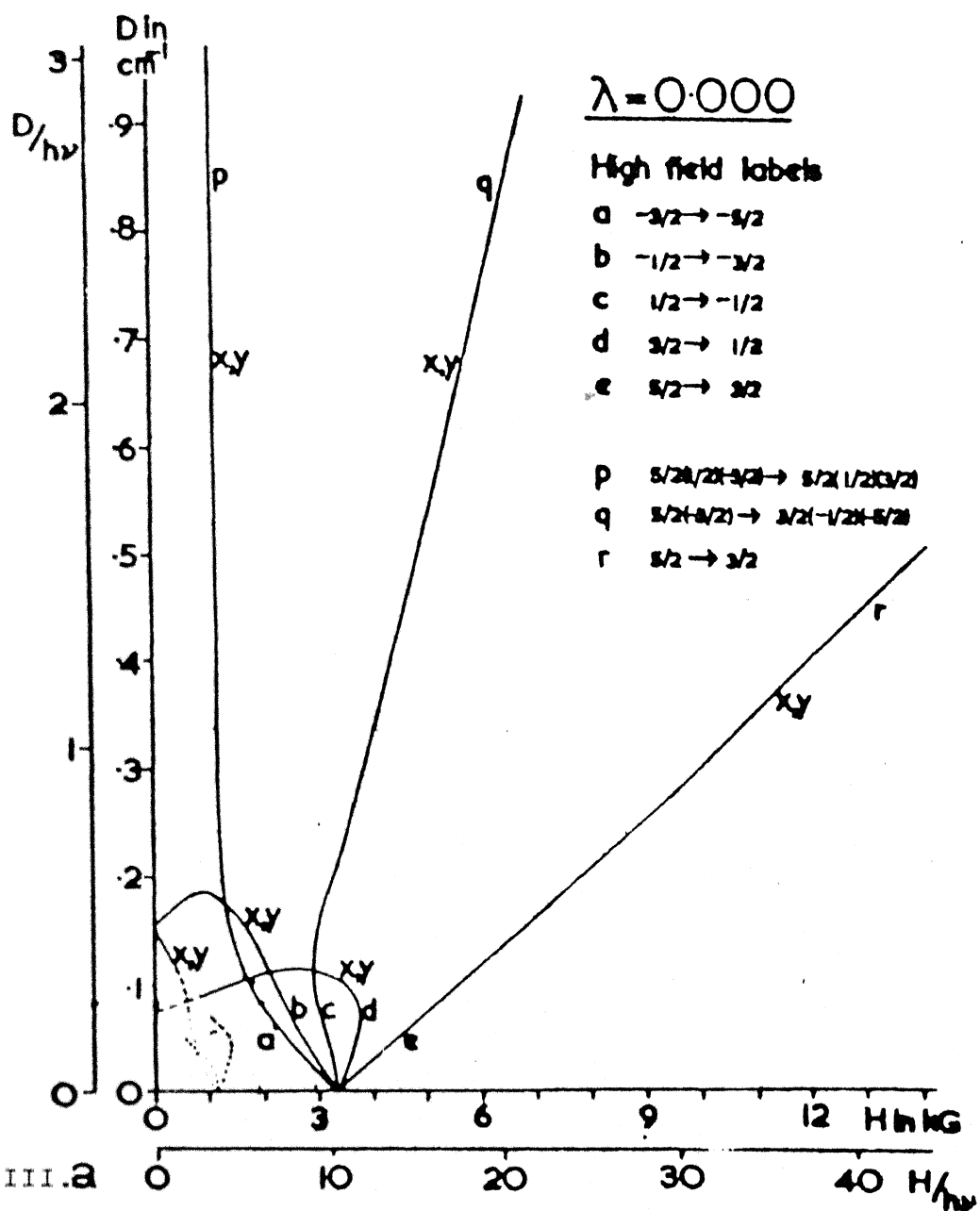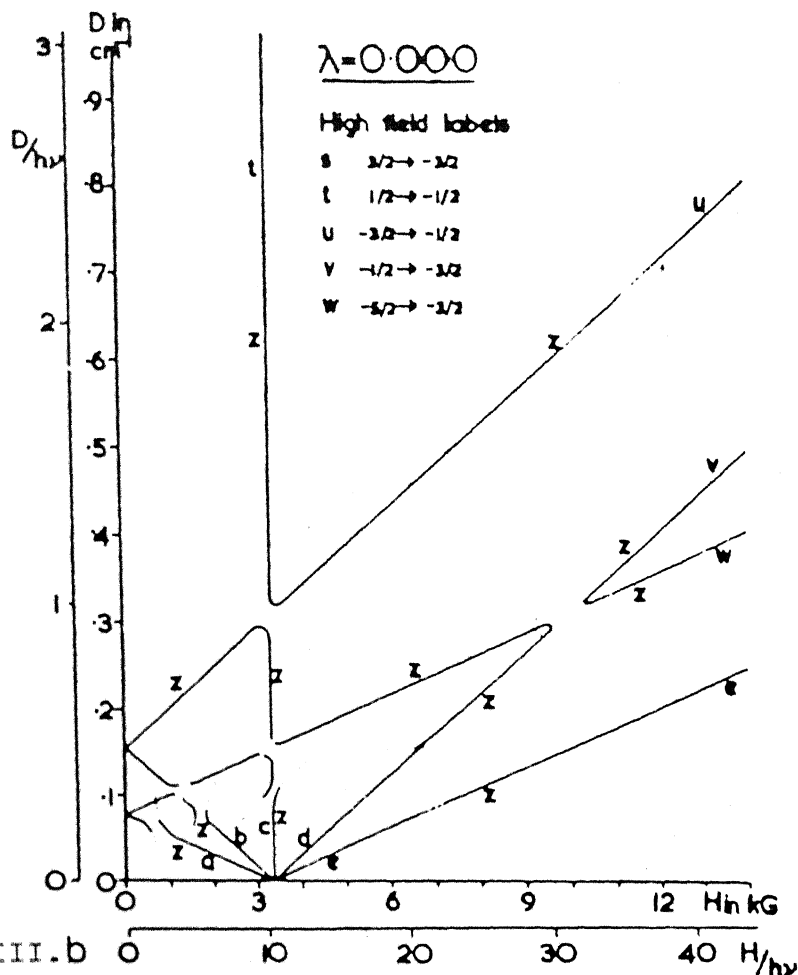
Fig. III.a

Fig.III. Predicted ESR transitions for $S = \frac{5}{2}$ as a function of the zero-field splitting parameter D against a function of the magnetic field in kilogauss for $\lambda = 0.0$. The full, dashed, and dotted lines represent transitions with high, low, and zero transition probability, respectively. The inner set of axes refer to D versus H for a quantum of microwave energy ($h\nu$) of 0.310 cm⁻¹ (X-band). The same graphs are applicable to any microwave frequency for the parameters $D/h\nu$ versus $H/h\nu$ as indicated on the outer set of axes. The letter x, y, or z close to a line is the axis to which the magnetic field is parallel for that line. The arbitrary presentation of the figures in two sets a and b for a given value of lambda is to simplify what would otherwise be a complex diagram. The other letters used against some of the lines are to indicate what transitions those lines represent, in terms of the magnetic quantum numbers which would represent the upper and lower spin states at very high field. An additional magnetic quantum number in parentheses represents a state which adds appreciably to the wavefunction for that line.

is likely that the proximity of neighbouring manganese ion results in magnetic interaction and causing a single line to be observed at $g_{eff} = 2$. ESR spectra of these compounds at various temperatures could have given the authentic support for magnetic interaction but it could not be possible due to non-availability of facilities. However, some non-regular monomeric compounds, particularly aquocomplexes, give a similar spectrum. Thus it is clear that observation of a single line spectrum does not itself indicate a regular structure.[12]

III.2.4.2 Ru(III) Complexes

Electron spin resonance spectra of the powdered samples of some of the Ru(III) complexes were recorded at room temperature at X-band frequencies and spectra were calibrated using a sample of DPPH (g = 2.0036 ± 0.0003), which was taped to sample holder. The ESR spectra obtained were essentially of two types: (i) two featured spectra indicating axial symmetry e.g. [Ru(MPQ)Cl$_2$-(o-phen)].H$_2$O and (ii) three featured spectra indicating rhombic distortion from octahedral symmetry for [Ru(MPQ)$_2$Cl.DMF] and [Ru(MPQ)$_2$Cl(py)].H$_2$O (Fig. III.3). The g values, ground state wavefunction parameters, orbital reduction factors, energy level splitting parameters, energies of three Kramers eigen-states and calculated d-orbital energies are given in Tables III.8 and III.9.

Theory

The theory of electron spin resonance in the low spin $d^5(t_{2g}^5)$ configuration was first put forward by Stevens[28] and developed by Bleaney and O'Brien[29] for distorted octahedral environment. This was further discussed by Griffith[30] and applied to a number of complexes.[31-35] Details of the theory for octahedral complexes with symmetry lower than tetragonal is given below:

Wavefunctions

As t_{2g}^6 is a closed shell configuration, t_{2g}^5 may be regarded as an one hole state t_{2g}^p. The ground term is $^2T_2$ and in the strong field limit is t_2^5 $^2T_2$ which is the complementary term of t_2^1 $^2T_2$ with respect to t_2^6. The $^2T_2$ wavefunctions are:[36]

$$\left|^2T_2 \, d_{yz} \, \tfrac{1}{2}\right> = \left|d_{yz} +\right> \quad \left|^2T_2 \, d_{yz} -\tfrac{1}{2}\right> = \left|d_{yz} -\right>$$

$$\left|^2T_2 \, d_{xz} \, \tfrac{1}{2}\right> = \left|d_{xz} +\right> \quad \left|^2T_2 \, d_{xz} -\tfrac{1}{2}\right> = \left|d_{xz} -\right>$$

$$\left|^2T_2 \, d_{xy} \, \tfrac{1}{2}\right> = \left|d_{xy} +\right> \quad \left|^2T_2 \, d_{xy} -\tfrac{1}{2}\right> = \left|d_{xy} -\right>$$

However, since these wavefunctions are degenerate, we may choose any orthogonal set of linear combinations of these six basic functions with spatial parts given by expression (3.1):

$$-|1> = \frac{1}{\sqrt{2}} \left|d_{xz} + id_{yz}\right>$$

$$|-1> = \frac{1}{\sqrt{2}} \left|d_{xz} - id_{yz}\right>$$

$$\varepsilon_1 = id_{xy} = \frac{1}{\sqrt{2}} \left[|1> - |-1> \right]$$

$$\dots(3.1)$$

Crystal field interaction

In crystal field of very high symmetry, the orbital angular momentum degeneracy is only partially removed. Thus, the d_{xy}, d_{yz} and d_{xz} orbitals are degenerate in an octahedral crystal field. In crystal field of lower symmetry the orbital generacy is further removed. For example, a trigonal or tetragonal distortion from the octahedral symmetry will left the degeneracy of the d_{xy} orbital with respect of d_{xz} and d_{yz} giving rise to an orbital singlet and an orbital doublet. A crystal field of much lower symmetry will remove all the degeneracies. The change in symmetry from octahedral to trigonal or tetragonal symmetry can be present-ed by a term in the Hamiltonian, $\delta \bar{I}_z^2$. It can be shown that d_{xz}, d_{yz} and d_{xy} are eigenfunction of $\delta \bar{I}_z^2$ operator with eigenvalues $-\delta$, $-\delta$ and $+2\delta$, respectively. The energy difference being 3 (see Fig. III.c).

The operator required to remove the orbital degeneracy further is given by

$$\mathcal{H} = \varepsilon\,(\bar{I}_x^2 - \bar{I}_y^2) = \varepsilon/2\,(\bar{I}_+^2 + \bar{I}_-^2)$$

The d_{xz} and d_{yz} orbitals are eigenfunctions of $\varepsilon/2(\bar{I}_+^2 + \bar{I}_-^2)$ operator with eigenvalues -3ε and $+3\varepsilon$; the energy difference being 6ε (Fig. III.c).

Spin orbit interaction and the energy matrix

Ignoring the configurational mixing of the excited states into the ground state, we now consider the spin orbit coupling

interaction and the crystal field distortion interaction for the basic set of wave functions (Eq. 3.1). The appropriate Hamiltonian operator is given by

$$\mathcal{H} = \lambda \cdot \bar{1} \cdot \bar{S} + \bar{1}_z^2 + \varepsilon/2 \, (\bar{1}_+^2 + \bar{1}_-^2) \qquad \qquad .. \ (3.2)$$

For convenience we use $\Delta \, (=3\delta)$ and $V(= 6\varepsilon)$ and add a constant term $(- \frac{\Delta}{3})$ to the Hamiltonian operator such that the trace of the matrix is Δ for all values of λ and V. This results in choosing the Hamiltonian operator:

$$\mathcal{H} = \lambda \cdot \bar{1} \cdot \bar{S} + \Delta/3 \, (\bar{1}_z^2 - 1) + V/12 \, (\bar{1}_+^2 + \bar{1}_-^2) \qquad \qquad .. \ (3.3)$$

Then the matrix of low symmetry perturbation and the spin orbit coupling breaks up into two identical submatrices which are shown in Table III.a.

Table III.a   Matrix of spin orbit coupling and low symmetry field

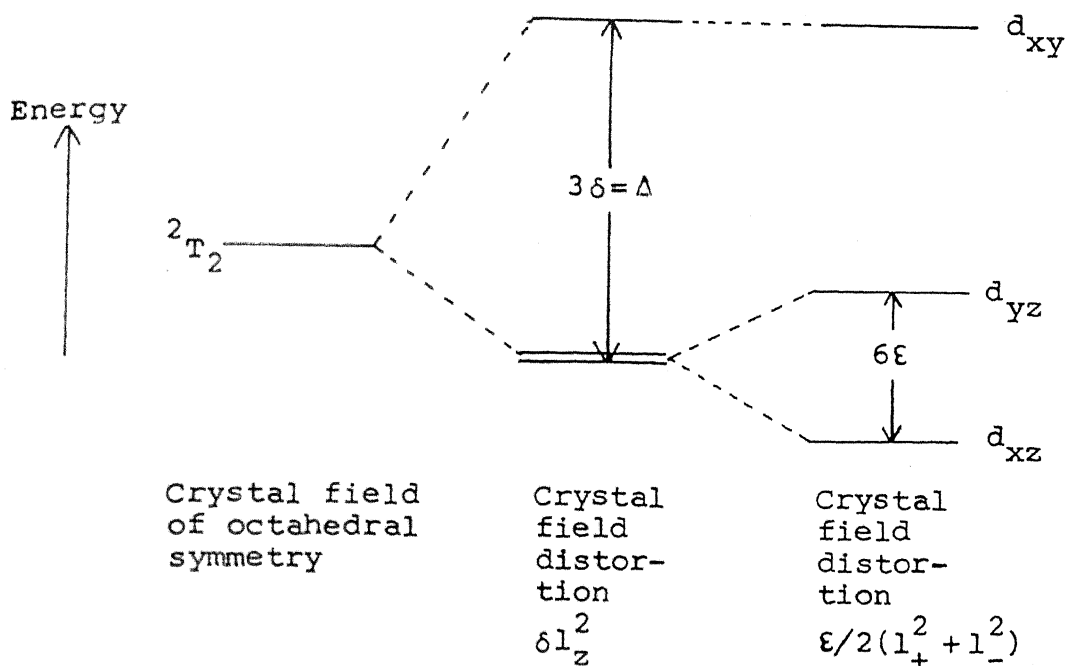|	$\lvert 1 +\rangle$ (or $\lvert -1 -\rangle$)	$\lvert \varepsilon_1 -\rangle$ (or $- \lvert \varepsilon_1 +\rangle$)	$\lvert -1 +\rangle$ (or $\lvert 1 -\rangle$)
$\lvert 1 +\rangle$ (or $\lvert -1 -\rangle$)	$\lambda/2$	$\lambda/\sqrt{2}$	$V/2$
$\lvert \varepsilon_1 -\rangle$ (or $- \lvert \varepsilon_1 +\rangle$)	$\lambda/\sqrt{2}$	Δ	0
$\lvert -1 +\rangle$ (or $\lvert 1 -\rangle$)	$V/2$	0	$-\lambda/2$

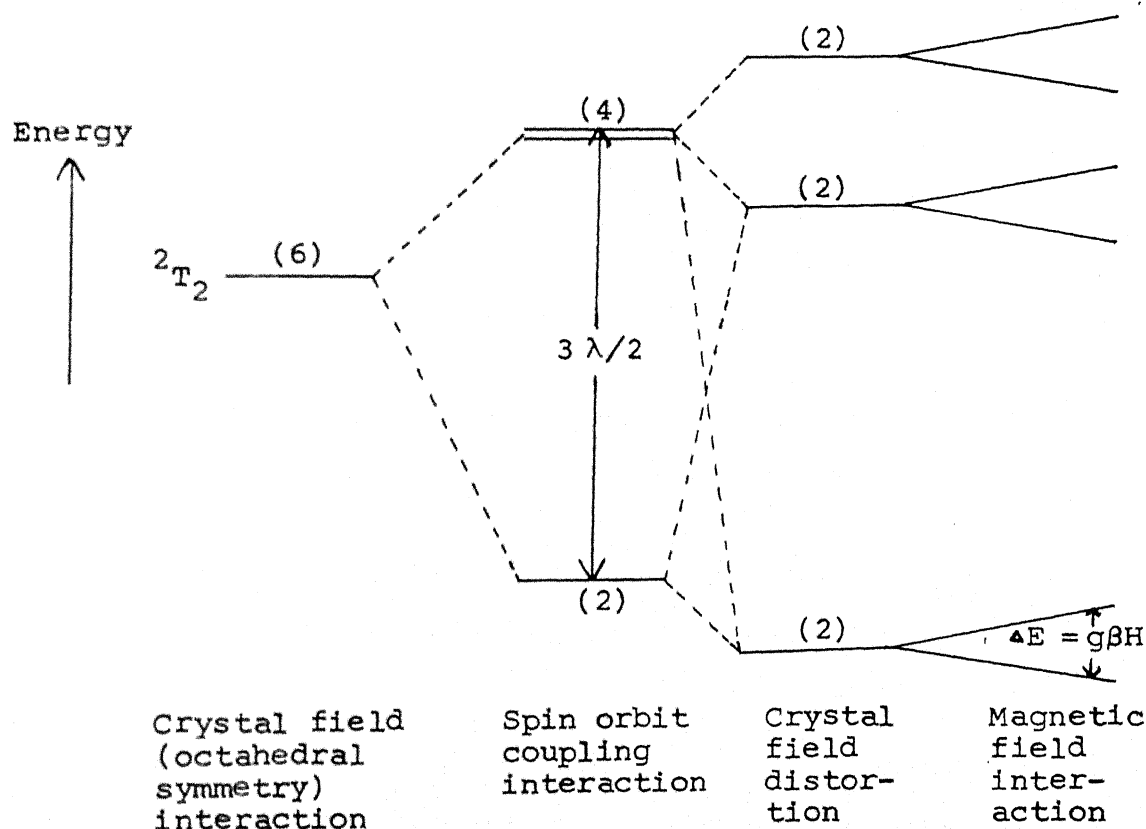Fig.III.c Splitting of $^2T_2$ term in a low symmetry crystal field.

Fig.III.d Spin orbit interaction, crystal field distortion inter-
action and magnetic field perturbation showing diagram-
matically (number in parentheses give total degeneracy)

The energy level diagram for the $^2T_2$ term of $d^5(t_{2g}^5)$ under the combined influence of low symmetry field, spin orbit, and magnetic field perturbation is given in Fig. III.d.

As indicated in Fig. III.b the combined effects of low symmetry field and spin-orbit interaction resolves the six-fold degeneracy of the $^2T_2$ term producing three well separated Kramers doublets. Δ is defined as the orbital splitting of the $^2T_{2g}$ term by the axial component of the ligand field, in the absence of spin orbit coupling. Δ is positive if the orbital singlet (i.e., $t_0 = d_z^2 = |0\rangle$ in trigonal or d_{xy} in tetragonal symmetry) lies lowest. This corresponds to a ^2E ground state for a $d^5(t_{2g}^5)$ system.

A general form of the ground state Kramer's doublet in which resonance is observed may be written as

$$\Psi = A \left|1+\right\rangle + B\left|\varepsilon_1-\right\rangle + C\left|-1+\right\rangle$$

$$\Psi' = A \left|-1-\right\rangle - B\left|\varepsilon_1+\right\rangle + C\left|1-\right\rangle \qquad \ldots (3.4)$$

where $\Psi = i\Psi^*$ and

$$A^2 + B^2 + C^2 = 1 \qquad \ldots (3.5)$$

where A, B and C are functions of λ, Δ and V.

Magnetic field interaction

The Kramer's doublet will be split by the magnetic field (Fig. III.d) interaction. Assuming that the magnetic field

mixing of the excited states into the ground state as negligible, the first order interaction can be represented by

$$\mathcal{H} = \beta \bar{H} (K\bar{I} + 2\bar{S})$$ .. (3.6)

where K is known as orbital reduction factor.[37-39] This parameter takes electron delocalization or covalency into account and is expected to be $\leqslant 1.0$.

Considering first the effect of magnetic field parallel to z-axis, we get zero matrix elements between Ψ and Ψ' and

$$\langle \bar{\Psi} | (K\bar{I}_z + 2\bar{S}_2) | \Psi \rangle = -\langle \bar{\Psi}' | (K\bar{I}_z + 2\bar{S}_z) | \Psi' \rangle$$

$$= K(A^2 - C^2) + A^2 - B^2 + C^2 \quad .$$

The energy separation of the Kramer's doublet as a result of the magnetic interaction gives

$$g_z = 2 \left[K(A^2 - C^2) + A^2 - B^2 + C^2 \right]$$ .. (3.7)

In a similar way if matrix elements of $(K\bar{I}_x + 2\bar{S}_x)$ and $(K\bar{I}_y + 2\bar{S}_y)$ for the magnetic field parallel to x-axis and y-axis, respectively are considered, one gets

$$g_x = 2 \left[2AC - B^2 + KB(C-A)\sqrt{2} \right]$$ .. (3.8)

$$g_y = 2 \left[2AC + B^2 + KB(C-A)\sqrt{2} \right]$$ .. (3.9)

Change of sign of any pair of these equations produces the physical results.[32]

Scope and Limitations of the Present Theory

(i) Assumptions

In major assumption made in the present theory is that only the $^2T_2$ ground term need be considered i.e., only the octahedral t_{2g} orbitals need be included in the basis set. This approximation could lead to serious errors if the crystal field or the spin-orbit interaction introduces configurational mixing of the excited states into the ground states. For example, in the intermediate crystal field for the d^5 ion, the $^4T_1$ state is sufficiently low in energy to give rise to considerable spin orbit mixing in the $^2T_2$ state. Large values of spin orbital coupling constant of the second and third row transition elements may favour such types of mixing.

It was assumed that there is equal bonding between d_{xy}, d_{xz} and d_{yz} and the appropriate ligand orbitals. This assumption is valid only when the crystal field distortions are small. For systems with low symmetry the anisotropy in the value of K must be taken into account.

The magnetic interaction matrix elements between higher states is also ignored. While interpreting the esr results these approximations should also be considered.

(ii) <u>Orbital reduction factor</u>

Orbital reduction factor 'K' is defined as[37]

$$K = \frac{\langle \phi | \bar{L} | \phi \rangle}{\langle d | \bar{L} | d \rangle}$$

where ϕ represents the real molecular orbital and d represents the pure d orbital of the metal. Thus the metal ligand orbital mixing, that is covalence, was explicitly introduced. In such molecular orbitals the unpaired t_{2g} electron of the metal may reside partly on the ligands, leading to a reduced orbital contribution of these electrons to the total angular momemtum. Thus K represents the effects of modifying metal d-wavefunctions by substituting for the angular momentum operator L, the reduced operator K L . The quantity K may be regarded as a parameter which describes the "degree of molecular orbital formation," the electron delocalisation parameter, or simply the covalence factor.

Considering delocalization to be a reality, $\langle \phi | \bar{L} | \phi \rangle$ should be less than $\langle d | \bar{L} | d \rangle$ thus making $K < 1.0$. Assuming that the unpaired electron spends atleast 50% of its time in the metallic d-orbitals, K should lie in the range $0.75 < K < 1.00$.[38] From the point of view of chemical bonding K seems to be very important parameter to be considered. However, all attempts to connect this to spin orbit coupling constant (λ/λ_o) or electron repulsion parameters (B/B_o) and to the π-acceptor properties of the ligand was failure.[39,40] It has been pointed out that

within the frame work of the present theory, care should be taken in interpreting K as covalency parameter as many factors are responsible.[32,39,41,42]

Within the t_{2g} manifold, only π-bonding orbitals can be found, so that the value of K above should be just $K_{\pi\pi}$;[37] There is another K factor, namely $K_{\pi\sigma}$, describing the reduced matrix elements of the orbital angular momentum operator between the wavefunctions of the t_{2g} set with the higher lying e_g set. This parameter is assumed to be small because the second order Zeeman effect contribution is assumed to be negligible. But if spin orbit interactions (which involves the angular momentum operator) mixes the excited (e_g) states into the ground (t_{2g}) states, then the above approximations of K are no longer strictly correct.

The assumption of equal bonding between the d_{xy}, d_{xz} and d_{yz} and the appropriate ligand orbitals gave rise to an isotopic K value. Gerloch and Miller[39] pointed out that in symmetry lower than cubic it is not justified to take a single K value for the interpretation of magnetic properties.

In addition, the presence of charge transfer states also influence the g-tensors. These results from the transfer of an electron from the ligands to the metal orbitals (for example, a π $t_{2g} \rightarrow dt_{2g}$ transfer). The latter orbitals are a mixture of metallic d-orbitals and ligand orbitals, so that spin orbit coupling can mix some of the charge transfer states into the ground state. Owen and Thornley[37] pointed out that the inclusion

of charge transfer states leads to positive contribution to the K factor. This is particularly important for second and third row elements where the charge transfer states have lower energies than most crystal field states.[43]

Method of Solution

If V/λ and Δ/λ in Table III.a are known, one can find the eigenvalues and eigenvectors of the matrix and thus predict the parameters of the resonance spectrum. Since, in practice, it is not possible to know this accurately, one has to work in the backward direction. From the knowledge of experimental g values (they are moduli of g_x, g_y and g_z Eqns. 3.7, 3.8, 3.9) A, B, C and K are calculated. As Ψ and Ψ' are solutions of the secular Eqns. 3.10, 3.11 and 3.12 associated with the matrix in Table III.a, Δ/λ, V/λ and E/λ can be calculated (there E is the energy of the ground state Kramer's doublet). The secular Equations are

$$(\lambda/2 - E)\ A + (\lambda//\overline{2})\ B + (V/2)\ C = 0 \qquad \text{.. (3.10)}$$

$$(\lambda//\overline{2})\ A + (\Delta - E)\ B = 0 \qquad \text{.. (3.11)}$$

$$(V/2)\ A + (-\lambda/2 - E)\ C = 0 \qquad \text{.. (3.12)}$$

Knowing V/λ and Δ/λ the matrix in Table III.a can be diagnolised from which one can obtain the three Kramer's eigenstates and their energies in terms of spin orbit coupling constant (λ) of the complex. For d^5 system one must change sign of λ, V and Δ

because these calculations so far was for a d^1 hole system.

A normal esr measurement does not determine the sign of the g_i components; nor it is possible to accurately determine the correspondence between the experimental g values and g_x, g_y and g_z components of g-tensor.[44] One must, therefore, consider all possible combinations for acceptable results. For axially symmetric molecules g_z is assigned to the unique component and only eight possible sign combinations were taken, while for molecules with lower symmetry there are forty eight possible combinations to be considered.

Computer Program

Equations (3.7) to (3.9) and (3.5) were simultaneously solved for A, B, C and K by using Newton-Raphson method. The four equations may be written in the form

$$f_i(x) = 0 \qquad i = 1, 2, 3, 4$$

where $x = [x_1, x_2, x_3, x_4]^t$, as follows:

$$f_1(x) = 2\,x_1x_3 - x_2^2 + x_4x_2\,(x_3 - x_1)/\sqrt{2} - g_x/2 \qquad \text{.. (3.13)}$$

$$f_2(x) = 2\,x_1x_3 - x_2^2 + x_4x_2\,(x_3 + x_1)/\sqrt{2} - g_y/2 \qquad \text{.. (3.14)}$$

$$f_3(x) = x_1^2 - x_2^2 + x_3^2 + x_4(x_1^2 - x_3^2) - g_z/2 \qquad \text{.. (3.15)}$$

$$f_4(x) = x_1^2 + x_2^2 + x_3^2 - 1 \qquad \text{.. (3.16)}$$

(Here x_1 = A; x_2 = B; x_3 = C and x_4 = K).

The computational method consists of following steps:

(1) Choose a starting vector $x_h = x_o$ $[x_{10}, x_{20}, x_{30}, x_{40}]$, where x_o is hopefully near a solution α.

(2) Solve the system of linear equations:

$$\emptyset(x_h)\, \delta_h = -f(x_h)$$

where

$$\emptyset_{ij}(x_h) = \frac{\delta f_i}{\delta x_j}(x_h) \qquad \begin{aligned} i &= 1,\ 2,\ 3,\ 4 \\ j &= 1,\ 2,\ 3,\ 4 \end{aligned}$$

and $f(x_h) = [f_1(x_h),\ f_2(x_h),\ f_3(x_h),\ f_4(x_h)]^t$, for the increment vector

$$\delta_h = [\delta_{1h},\ \delta_{2h},\ \delta_{3h},\ \delta_{4h}]^t\ .$$

(3) Update the approximation to the root for the next interation

$$x_{h+1} = x_h + \delta_h\ .$$

(4) Check for possible convergence to a root. One such test might be

$$|\delta_{ih}| < \varepsilon_2 \qquad i = 1,\ 2,\ 3,\ 4 \qquad\qquad\qquad\ ..\ (3.17)$$

if (3.17) is true for all i, then x_{h+1} is taken to be the root. If (3.17) failed for any i, then the process is repeated starting with step 2. The iterative process is continued until test (3.17) is passed for some h, or h exceeds some specified upper limit.

In the computer programme the element of the augmented matrix

$$A \left[\emptyset(x_h) \mid -f(x_h) \right]$$

are evaluated and the system of linear equations in step (2) is solved by using Gauss-Jordan complete elimination method using maximum pivot strategy.

The choice of a starting vector in step (1) is very important. The normalisation condition (Eqn. 3.5) can be used as a guide for selecting the initial values of A, B and C. Griffith[45] has shown that the coefficients of the wavefunctions of the ground state Kramer's doublet for a d^5 system under the group D_4 should correspond to

$$A = \sqrt{2/3} = 0.870; \quad B = \sqrt{1/3} = 0.578; \quad C = 0.000$$

The use of above values of A, B and C gives fast convergence. We have used four sets of initial values as given below:

(I) A = 0.87   B = 0.58   C = 0.00   K = 1.00

(II) A = 0.15   B = 0.98   C = 0.00   K = 1.00

(III) A = 0.58   B = 0.58   C = 0.58   K = 0.75

(IV) A = 0.50   B = 0.707   C = 0.50   K = 0.50

If convergence occurs in more than one case then they yield identical results. All solutions where the value of K was out side the range 0.75 – 2.00 were rejected.

Secular Equations (3.10-3.12) were then solved and the eigenvalues of the matrix in Table III.a were determined by using Jacobi's method of matrix diagonalisation. A DEC-1090 system was used throughout this work.

The computer program was then tested by using literature reported data and found satisfactory.[34]

Choice of Solution

For system with axial symmetry there are eight possible combinations of g-values out of which convergence occurs in more than one case. For molecules showing three featured spectra the fourty eight combinations usually lead to six solutions with identical K values. These solutions differ only in their of the real one electron d functions and in the values of coefficients A, B and C. In such cases one can make a choice by taking the pair corresponding to $g_z \approx 2.0$ (fits 1 & 2 in Table III.8).

As a first approximation, the value of K was used for selecting one or more possible solutions. If the unpaired electron spends at least 50% of its time in metallic d-orbitals, the value of K show lie in the range $0.75 < K < 1.00$. However, a large value of K can be obtained if the assumption made in the theory are not strictly valied.[31,32,39,42] We have considered the value of K in the range $0.75 - 2.00$ with this restriction on the values of K, results of the calculation are shown in Table III.8.

In the ground state of the molecules, esr absorption should correspond to transition between the lowest Kramer's doublet levels, as otherwise the parameters derived from the theory are physically unreal. Our calculations show that, for a given combination of g-values of the complexes in Table III.8, the solution that corresponds to the lowest energy of the ground state Kramer's doublet (E) also yield the smallest value of K. The tetragonal distortion, Δ, is assumed to be larger, than rhombic distortion, V, which seems reasonable if we consider the structure of the complexes examined.

Discussion

The value of orbital reduction factor, K, should, in principle, be a measure of covalency. But for many of the complexes studied the value of K is more than 1.0. This is quite surprising for complexes with π-bonding ligands like triphenylphosphine and triphenylarsine which are shown to form strong metal-ligand covalent bonds. Therefore, a direct correlation of orbital reduction factor and covalency was not possible to make from the available data. For the complexes studied here, the value of K is in the range 0.95 - 1.21. The value 0.953 of K for the complex $[Ru(MPQ)Cl_2(o\text{-phen})].H_2O$ is expected one as o-phenanthroline is known to behave as π-bonding ligand and form strong metal-ligand covalent bonds. The value of K more than 1.0 is also not surprising as many other factors are responsible for the variation in the value of K.[31,32,39,42]

For example, it has been shown[46,47] that by considering $t_2^4(^3T_1)e$ and $t_2^4(^1T_2)e$ configurations mixed into the $t_2^5(^2T_2)$ by electrostatic interactions, one can modify the high values of K by a substantial amount. Moreover large axial distortion will split up the ground triplet into a double and a singlet term. This further increases the possibility of configurational mixing of the ground term with higher energy terms of the same symmetry. An important contribution to the large values of K is, probably, the presence of low lying charge transfer states. Since the 4d or 5d electrons are less tightly bound to the metal atom, the molecular formation occurs readily and as a result the charge transfer (CT) states have lower-energy than most crystal field states.[43]

For axially symmetric molecule, [Ru(MPQ)Cl$_2$(o-phen)]·H$_2$O, there are two acceptable fits, the fit (1) shows the sign of g_y positive and that of g_x and g_z negative (B > A, C) and the results show that the hole is in the $t_2^o(d_{xy})$ orbital. Similar assignments have been reported for β-diketonate complexes of Ru(III).[34]

For the complexes [Ru(MPQ)$_2$Cl·DMF] and [Ru(MPQ)$_2$Cl(py)]·H$_2$O the two possible fits were limited to the following ($g_1 = -g_x$, $g_2 = g_y$, $g_3 = g_z$) or ($g_1 = g_y$, $g_2 = -g_x$, $g_3 = g_z$). These solutions are equivalent with each other, differing only in choice of x and y axes, in other words, defferring in the signs of both the coefficient C and V/λ values and it is difficult to reject any of the two. Assignments giving a negative V/λ values

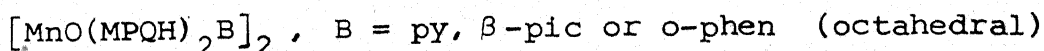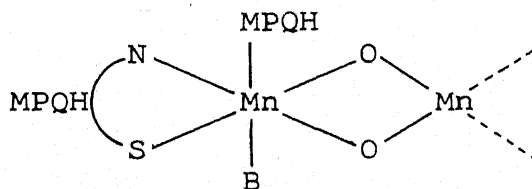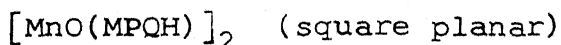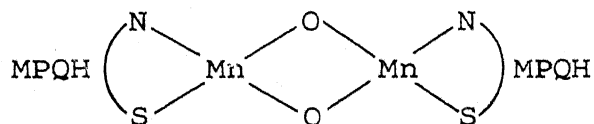have been chosen and reported for $[RuX(NH_3)_5]^{2+}$ (X = Cl or Br).[48]
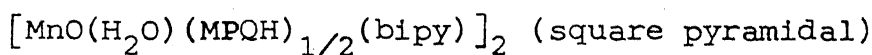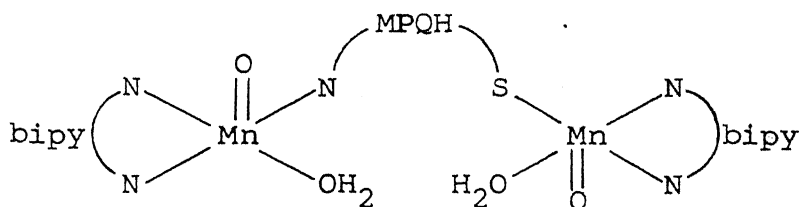
The orbital energies of some of the complexes are given in Table III.9. For the complexes with three distinct components, two fits were found and results are not very much different from each other. The highest lying orbital is d_{xy} and the ground state may be either (a) d_{yz} or (b) d_{xz}. It is difficult to decide between the two possibilities. The positive value of Δ/λ found in this work means that the d_{xy} orbital lies higher in the energy than d_{xz} and d_{yz} orbitals. Thus supporting the order of d-orbitals energies listed in Table III.9.

III.3 Conclusion

On the basis of analytical, magnetic, conductivity and spectroscopic (i.r., u.v., & visible and e.s.r.) studies, the following structures are proposed for Mn(II), Ru(III) and Rh(III) complexes.

III.3.1 Oxo-manganese Complexes

$[MnO(MPQH)]_2$ (square planar)

$[MnO(MPQH)_2B]_2$, B = py, β-pic or o-phen   (octahedral)

$$[\text{MnO(H}_2\text{O)(MPQH)}_{1/2}(\text{bipy})]_2 \quad (\text{square pyramidal})$$

In the structure of $[\text{MnO(MPQH)}_2(\text{o-phen})]$, either one ligand molecule MPQH or o-phen acts as unidentate ligand on the basis of IR, it is difficult to ascertain either possibility and it is also difficult to decide whether unidentate MPQH is coordinated through N or S.

III.3.2 Ru(III) Complexes

The complexes $[\text{Ru(MPQ)}_2\text{Cl.DMF}]$ and $[\text{Ru(MPQ)}_2\text{Cl(py)}].\text{H}_2\text{O}$ show rhombic distortion as $g_x \neq g_y \neq g_z$ for these complexes and the complex $[\text{Ru(MPQ)Cl}_2(\text{o-phen})].\text{H}_2\text{O}$ is axially symmetric molecule as $g_x = g_y \neq g_z$.
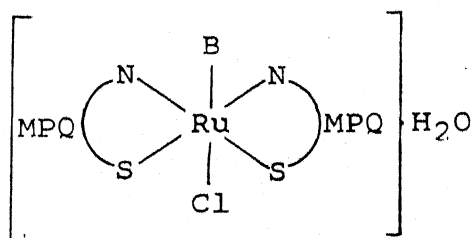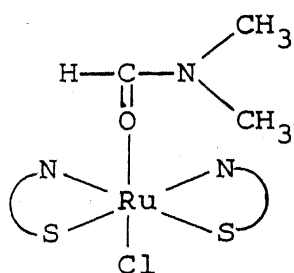
B = H$_2$O, py, β-pic or imzH
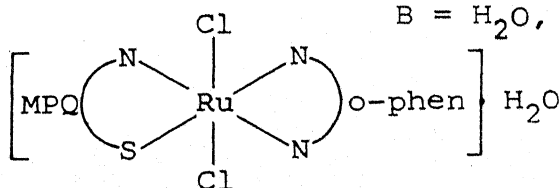
III.3.3 Rh(III) Complex

The complex $[Rh(MPQ)(MPQH)Cl_2].2H_2O$ possesses distorted octahedral geometry:
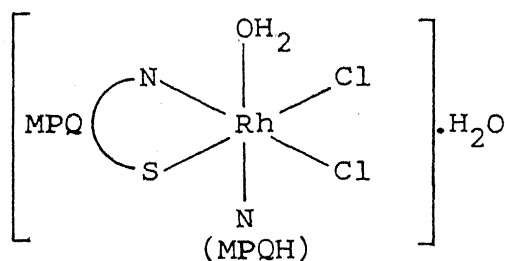
Table III.1. Analytical and magnetic moments data

Compound[a]	M.P. (°C)	Found (Calc.), %					μ_{eff}* (B.M.)
		Mn	S	C	H	N	
MnO(MPQH)	235	17.1 (16.9)	9.6 (9.8)	52.0 (51.7)	3.1 (3.1)	8.8 (8.6)	4.24
MnO(MPQH)$_2$(py)	240	8.5 (8.4)	9.8 (9.7)	60.1 (60.2)	4.0 (3.8)	10.7 (10.6)	5.72
MnO(MPQH)$_2$(β-pic)	225	8.1 (8.2)	9.4 (9.5)	60.5 (60.7)	3.9 (4.0)	10.3 (10.4)	5.86
MnO(MPQH)$_2$(o-phen)	215	7.3 (7.2)	8.5 (8.4)	63.4 (63.2)	3.5 (3.7)	11.2 (11.1)	5.98
MnO(H$_2$O)(MPQH)$_{1/2}$(bipy)	240	15.0 (14.8)	4.4 (4.3)	54.9 (54.8)	4.1 (4.0)	11.1 (11.3)	6.08

a, All compounds are of brown colour.

*, Measured at 293 K and uncorrected for diamagnetism.

Table III.2. Analytical and magnetic data of complexes

Compound	Colour	M.P. (°C)	μ_{eff}* (B.M.)	Found (Calc.), %					
				M	S	C	H	N	Cl
[Rh(MPQ)(MPQH)Cl$_2$]2H$_2$O	Yellow	>290	D.M.	– (14.4)	9.1 (8.9)	46.8 (46.9)	3.1 (3.2)	8.0 (7.8)	10.0 (9.9)
[Ru(MPQ)$_2$Cl.DMF]	Violet	232d,	1.75	14.4 (14.1)	9.1 (8.9)	51.8 (52.0)	3.4 (3.5)	9.6 (9.8)	4.8 (5.0)
[Ru(MPQ)$_2$Cl(H$_2$O)]H$_2$O	Black	>290	1.82	15.1 (14.9)	9.2 (9.4)	50.3 (50.0)	3.3 (3.2)	8.5 (8.3)	5.0 (5.2)
[Ru(MPQ)$_2$Cl(py)]H$_2$O	Greenish black	290	2.10	13.4 (13.7)	8.6 (8.7)	53.5 (53.6)	3.5 (3.4)	9.3 (9.5)	5.0 (4.8)
[Ru(MPQ)$_2$Cl(β-pic)]	Brown black	210	2.07	13.6 (13.4)	8.4 (8.5)	54.3 (54.1)	3.4 (3.6)	9.1 (9.3)	4.9 (4.7)
[Ru(MPQ)Cl$_2$(o-phen)]-H$_2$O	Reddish brown	212	1.73	16.5 (16.2)	5.3 (5.1)	50.3 (50.1)	3.2 (3.0)	9.1 (8.9)	11.3 (11.4)
[Ru(MPQ)$_2$Cl(imzH)]H$_2$O	Sea-green	215	1.94	13.8 (14.0)	9.0 (8.9)	52.0 (51.8)	3.7 (3.6)	11.8 (11.7)	5.1 (4.9)

DM = diamagnetic

* At 20°C and uncorrected for diamagnetism;   d = decomposes.

Table III.3 Major IR bands of interest (in cm^{-1})

Compound	ν(NH)	ν(OH)	ν(CO)	Thioamide bands			
				I	II	III	IV
Ligand (MPQH)	3250m	–	1660s	1540s	1345s	1000s 980m	770s
MnO(MPQH)	3260m	–	1670s	1540s	1350w	995m 980w	765s
MnO(MPQH)$_2$(py)	3270s	–	1675s	1545s	1355w	985w	770s
MnO(MPQH)$_2$(β-pic)	3240–3275m	–	1675s	1540s	–	1000w	770s
MnO(MPQH)$_2$(o-phen)	3240–3260m	–	1675s	1540m	–	–	770s
MnO(H$_2$O)(MPQH)$_{1/2}$(bipy)	3240m	3450br	1680m	1530w	1340w	990s	765s

s = strong, m = medium, w = weak, br = broad

Table III.4   Comparison of IR bands of ligand (MPQH) and metal complexes (cm^{-1})

Compound	ν(NH)	ν(OH)	ν(C=O)	Thioamide bands			
				I	II	III	IV
MPQH	3250	–	1660s	1540s	1345s	1000s, 980m	770s
Rh(MPQ)(MPQH)Cl$_2$·2H$_2$O	3240–3260w	3500br	1700s	1520m	1330s, 1340w	1000w	770s
[Ru(MPQ)$_2$Cl·DMF]	–	–	1690s	1520m	1330m	1000m	780s
[Ru(MPQ)$_2$Cl(H$_2$O)]H$_2$O	–	3460br	1700s	1510m 1320s	1330s 1320s	1030w 990w	770s
[Ru(MPQ)$_2$Cl(py)]H$_2$O	–	3460br	1680s	1510s	1320s	1010m 990m	770s
[Ru(MPQ)$_2$Cl(β-pic)]H$_2$O	–	3400br	1690s,br	1505s	1310s	980m	790m 760s
[Ru(MPQ)Cl$_2$(o-phen)]H$_2$O	–	3400br	1690s	1510s	1320m	990w	770s
[Ru(MPQ)$_2$Cl(imzH)]H$_2$O	3340–3420br	–	1700s	1510m	1330m, 1320m	1000w	770s

Table III.5   Reflectance spectra of the complexes at room temperature

Compound	Band position λ_{max} (nm)	Assignments
MnO(MPQH)	300sh	IL
	340sh	CT
	570w,sh	$^6A_{1g}(^6S) \longrightarrow {}^4T_{1g}(^4G)$
MnO(MPQH)$_2$(py)	360sh	CT
MnO(MPQH)$_2$(β-pic)	460v,br	$^6A_{1g}(^6S) \longrightarrow {}^4T_{2g}(^4G)$
MnO(MPQH)$_2$(o-phen)	300sh	IL
MnO(H$_2$O)(MPQH)$_{1/2}$(bipy)	285sh	IL
	350w,sh	CT
	570w,sh	$^6A_{1g}(^6S) \longrightarrow {}^4T_{1g}(^4G)$

w = weak; v = very; br = broad; sh = shoulder.

Table III.6   Electronic spectra of complexes in methanol and typical g-values of some of the Ru(III) and Rh(III) complexes

Compound	Band position λ_{max} (nm)	Assignments	ESR Spectra			
			g_1	g_2	g_3	g
1	2	3	4	5	6	7
Ligand (MPQH)[a]	262	$\pi \rightarrow \pi^*$				
	295	$\pi \rightarrow \pi^*$				
Rh(MPQ)(MPQH)Cl$_2\cdot$2H$_2$O	265	IL				
	310sh	IL or CT				
[Ru(MPQ)$_2$Cl.DMF][a]	265	IL	2.74	2.25	1.79	2.29
	306	IL				
	465	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$				
	525	$^2T_{2g} \rightarrow {}^4T_{2g}$				
[Ru(MPQ)$_2$Cl(H$_2$O)]H$_2$O	295	IL				
	555	$^2T_{2g} \rightarrow {}^4T_{2g}$				
[Ru(MPQ)$_2$Cl(py)]H$_2$O	300	IL	2.32	2.14	2.01	2.16
	330	CT				
	415	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$				
[Ru(MPQ)$_2$Cl(β-pic)]H$_2$O	295	IL				
	430	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$				
	655	$^2T_{2g} \rightarrow {}^4T_{1g}$				

...contd.

Table <u>III.6</u> (contd.)

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1	2	3	4	5	6	7
$[Ru(MPQ)Cl_2(o\text{-}phen)]H_2O$	295	IL	2.23	2.23	1.95	2.14
	485	$^2T_{2g} \rightarrow {}^2T_{1g}$				
$[Ru(MPQ)_2Cl(imzH)]H_2O$	300	IL				
	565	$^2T_{2g} \rightarrow {}^4T_{2g}$				
	645	$^2T_{2g} \rightarrow {}^4T_{1g}$				

a, Spectra taken in DMF solvent.

$$g = \left[\frac{1}{3}g_1{}^2 + \frac{1}{3}g_2{}^2 + \frac{1}{3}g_3{}^2\right]^{1/2}.$$

Table III.7 ESR parameters of oxo-manganese(II) complexes

Compound	Absorption G	Linewidth G	g_{eff}	Axial Distortion D (cm^{-1})	$\lambda (= E/D)$ (cm^{-1})
$MnO(MPQH)_2(py)$	3300	250	2.00	–	–
$MnO(MPQH)_2(\beta\text{-pic})$	3300	250	2.00	–	–
$MnO(MPQH)_2(o\text{-phen})$	3300 1975	325 625	2.00	0.095	0.00–0.01
$MnO(H_2O)(MPQH)_{1/2}(bipy)$	3288 1875 4675	250 625 750	2.01	0.12	0.00–0.01

Table III.8   g Values, ground state wavefunction parameters, orbital reduction factors and energy level splitting parameters of ruthenium(III) complexes

Compound	Fit	g_x	g_y	g_z	K	A	B	C	V/λ	Δ/λ
$[Ru(MPQ)_2Cl.DMF]$	(1)	-2.25	2.74	1.79	1.209	0.768	0.639	0.047	0.193	0.243
	(2)	-2.74	2.25	1.79	1.209	0.768	0.639	-0.047	-0.193	0.243
$[Ru(MPQ)_2Cl(py)]H_2O$	(1)	-2.14	2.32	2.01	1.119	0.802	0.598	0.018	0.067	0.074
	(2)	-2.32	2.14	2.01	1.119	0.802	0.598	-0.018	-0.067	0.074
$[Ru(MPQ)Cl_2(o\text{-}phen)]H_2O$	(1)	-2.23	2.23	-1.95	0.953	0.902	0.996	0.0	0.0	0.640
	(2)	-2.23	2.23	1.95	1.104	0.798	0.603	0.0	0.0	0.099

Table III.9   Energies of three Kramers eigenstates and calculated d-orbital energies for the complexes

Compound	E/λ	E_1/λ	E_2/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$	d-Orbital order	Energies (λ cm^{-1})
$[Ru(MPQ)_2Cl.DMF]$	-1.093	0.326	0.525	1.419	1.618	yz < xz < xy	-0.177, 0.015, 0.162
						xz < yz < xy	-0.177, 0.015, 0.162
$[Ru(MPQ)_2Cl(py)]H_2O$	-1.026	0.444	0.508	1.470	1.534	yz < xz < xy	-0.058, 0.009, 0.050
						xz < yz < xy	-0.058, 0.009, 0.050
$[Ru(MPQ)Cl_2(o-phen)]H_2O$	-1.281	0.141	0.5	1.422	1.781	e (xz, yz) < b_2 (xy)	-0.21, 0.42
	-1.035	0.436	0.5	1.471	1.535	-do-	-0.33, 0.66

E is lowest energy of ground state Kramer's doublet.

LEGEND TO FIGURES

Fig. III.1 Infrared Spectra

1. $Ru(MPQ)_2Cl.DMF$

2. $Ru(MPQ)_2Cl(imzH).H_2O$

3. $Rh(MPQ)(MPQH)Cl_2.2H_2O$

4. $MnO(MPQH)_2(\beta-pic)$

Fig. III.2 Electronic Spectra

1. $Ru(MPQ)Cl_2(o-phen).H_2O$

2. $Ru(MPQ)_2Cl(H_2O).H_2O$

3. $Ru(MPQ)_2Cl(imzH).H_2O$

4. $Rh(MPQ)(MPQH)Cl_2.2H_2O$

5. $Ru(MPQ)_2Cl.DMF$

6. $Ru(MPQ)_2Cl(py).H_2O$

7. MPQH

Fig. III.3 ESR Spectra

1. $MnO(MPQH)_2(py)$

2. $MnO(MPQH)_2(\beta-pic)$

3. $MnO(MPQH)_2(o-phen)$

4. $MnO(MPQH)_{1/2}(bipy)(H_2O)$

5. $Ru(MPQ)_2Cl.DMF$

6. $Ru(MPQ)_2Cl(py).H_2O$

7. $Ru(MPQ)Cl_2(o-phen).H_2O$
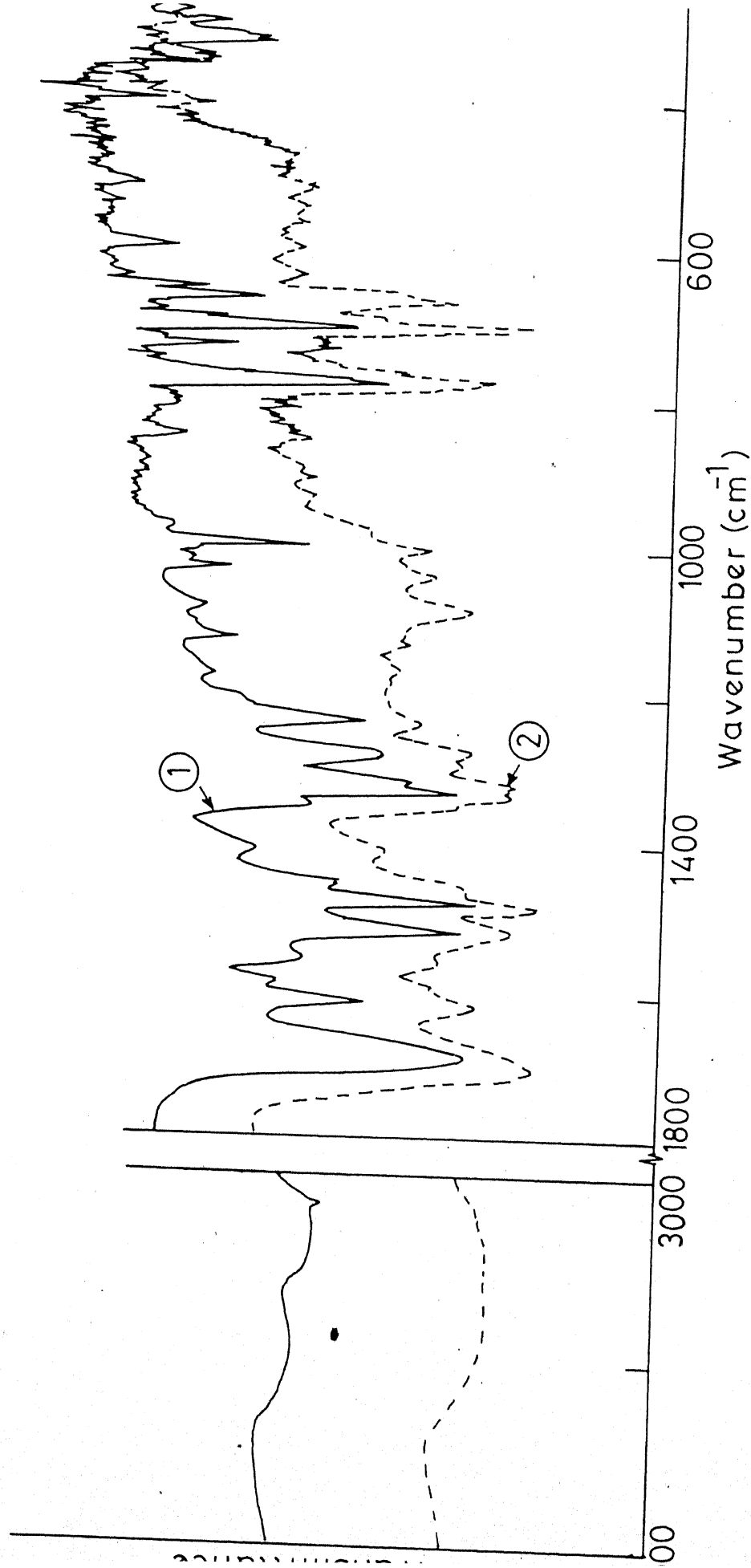
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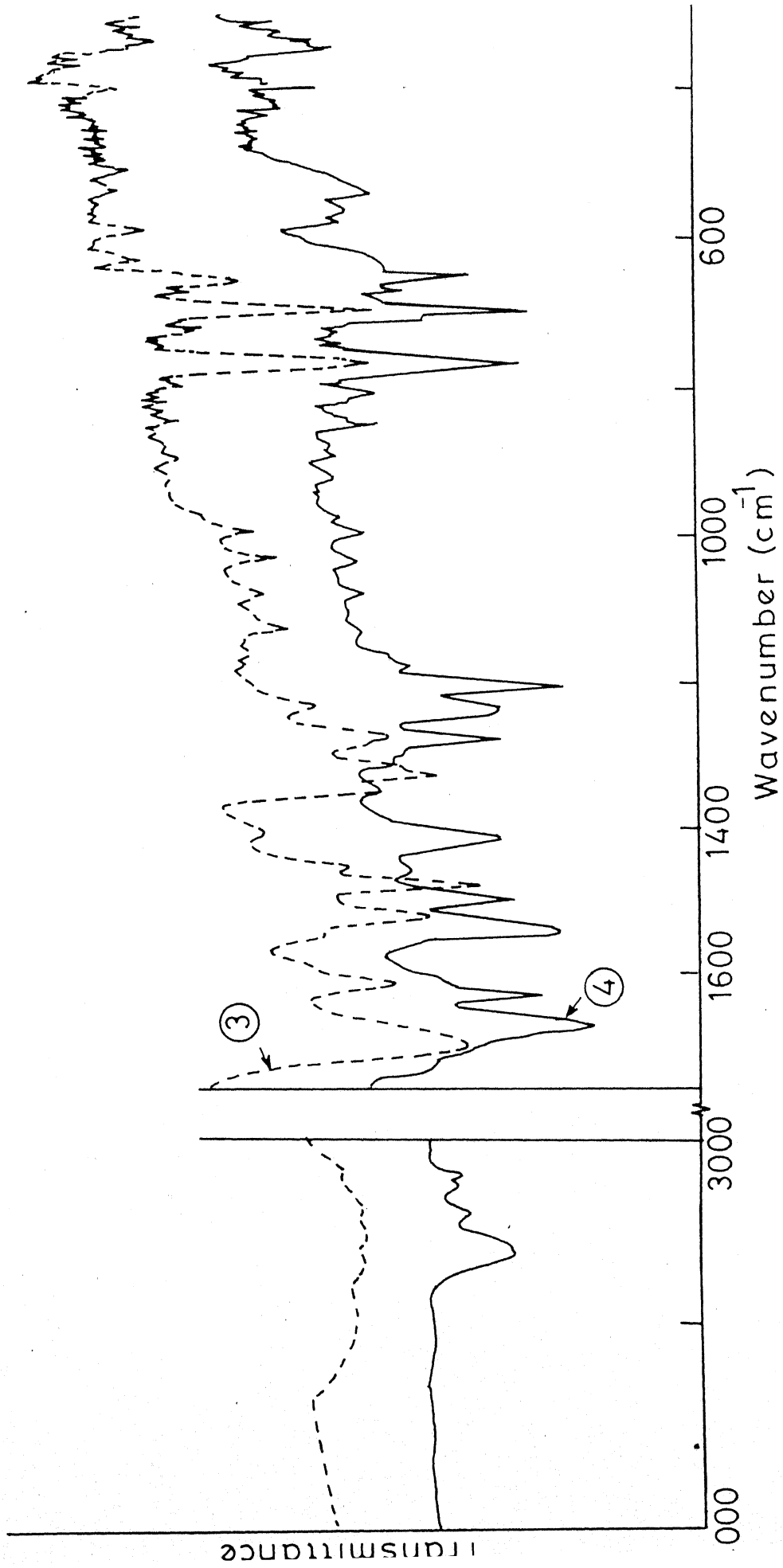
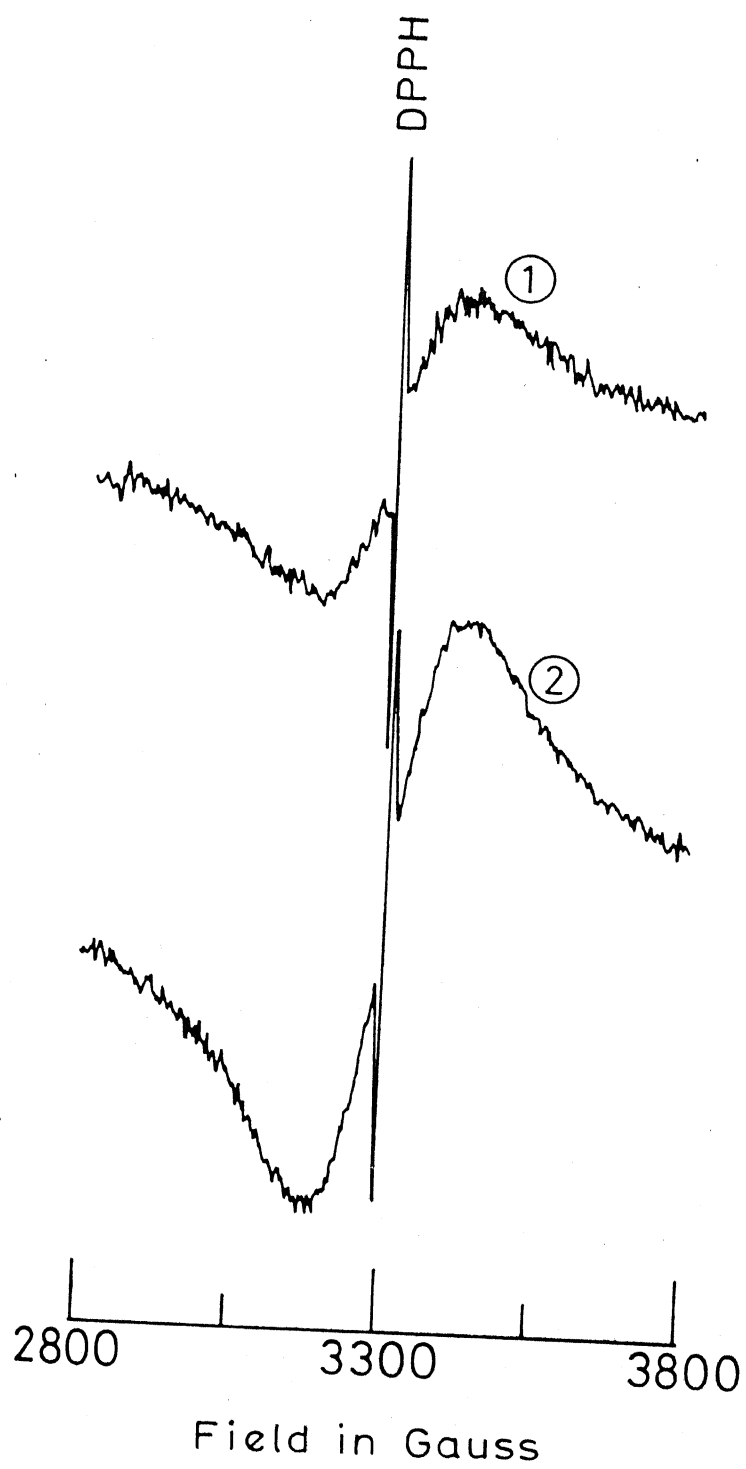Fig.III.2 IR Spectra
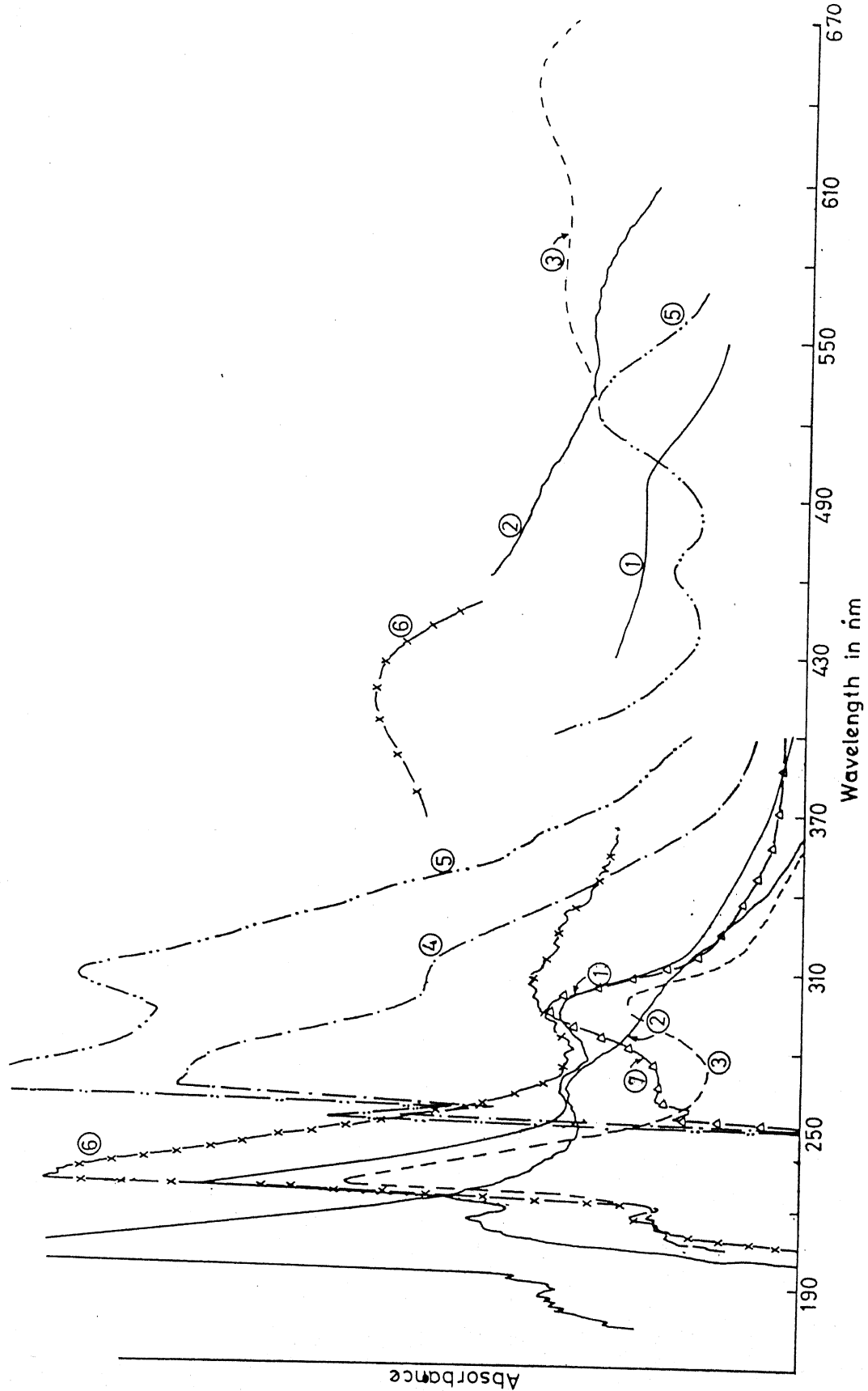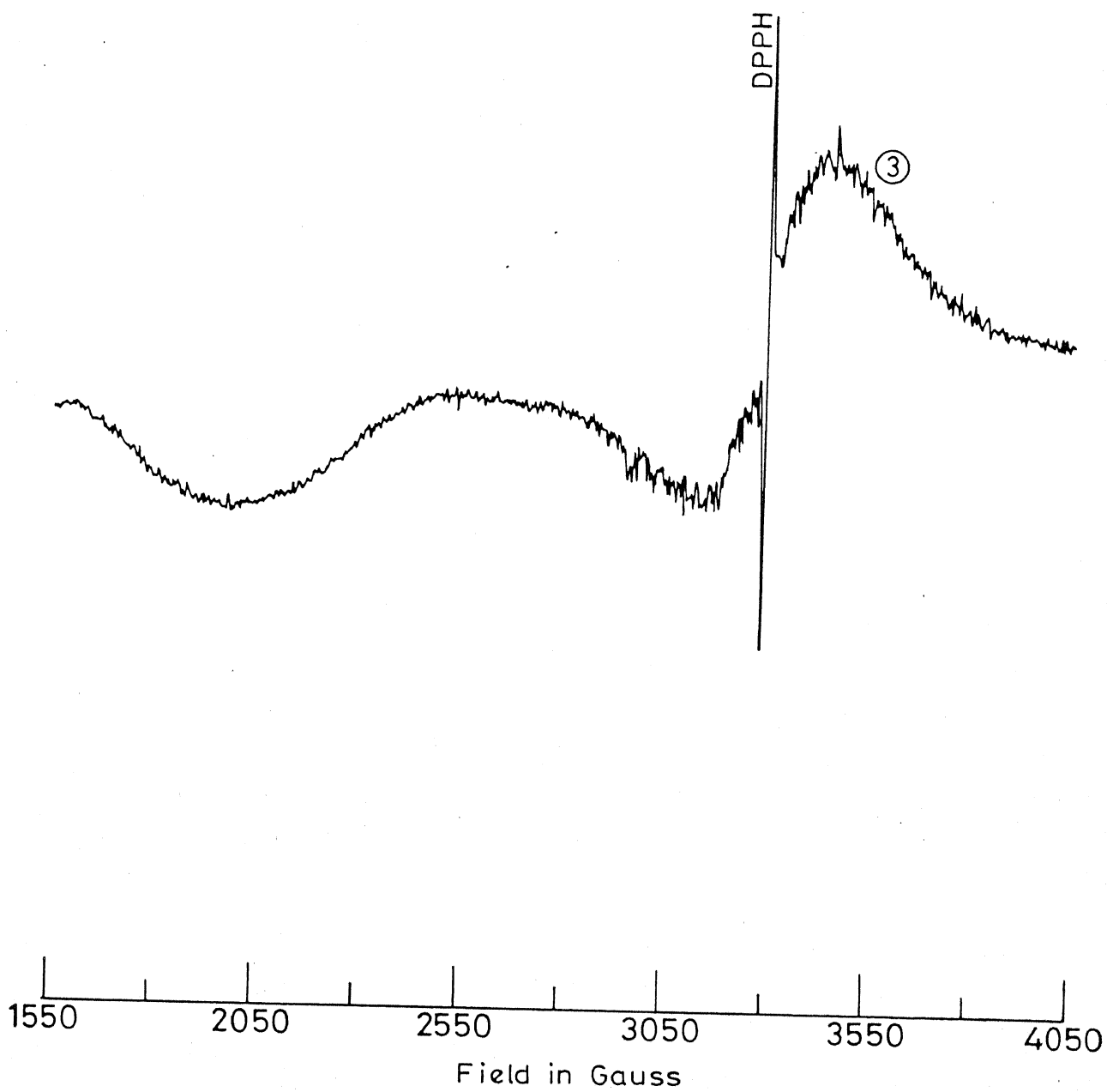
Wavelength in ńm

Fig. III.2 Electronic spectra

Absorbance

Fig. III.3 ESR spectra

Fig.III.3 ESR spectra

Fig.III.3 ESR spectra

Field in Gauss

④

DPPH

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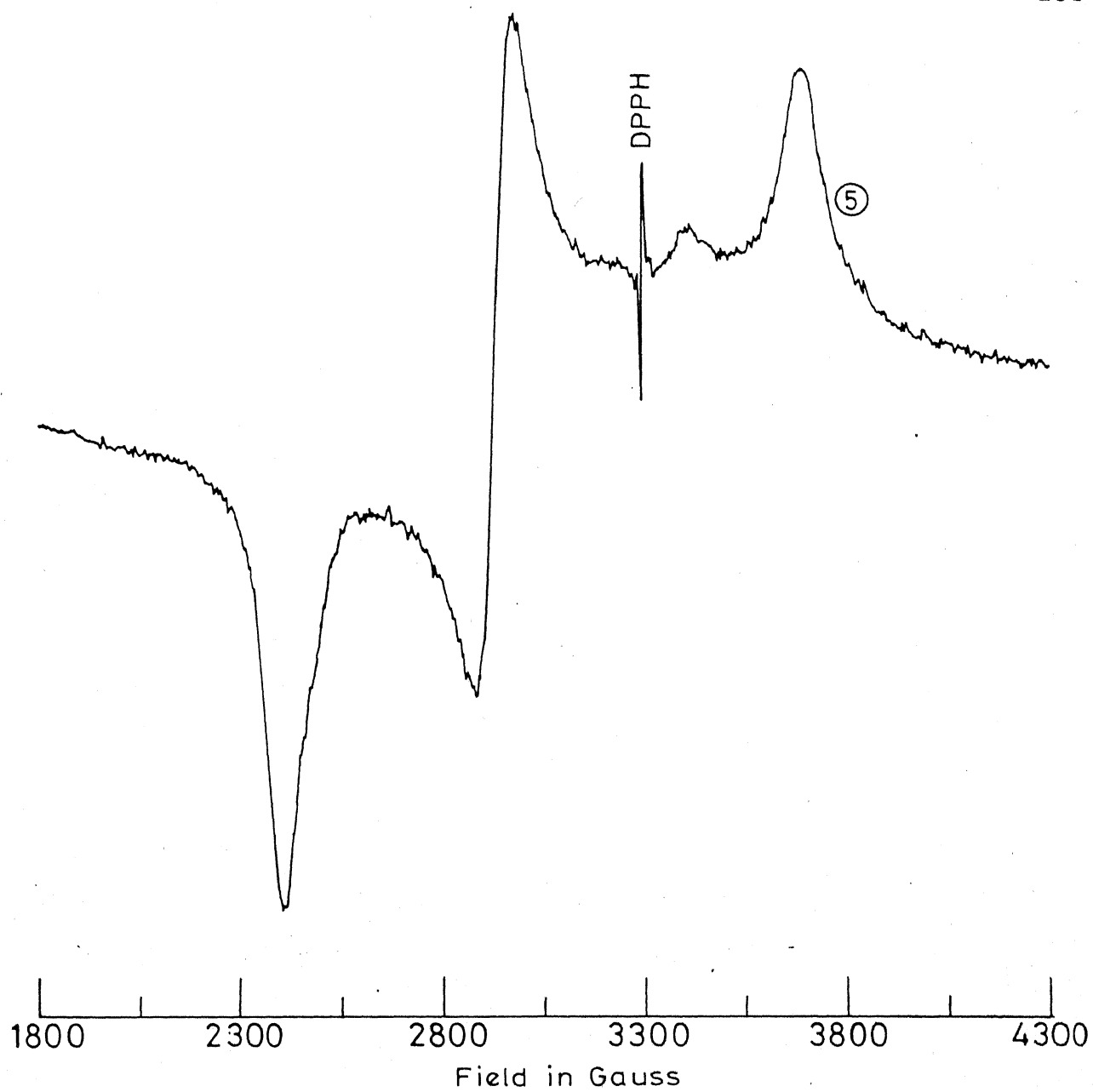
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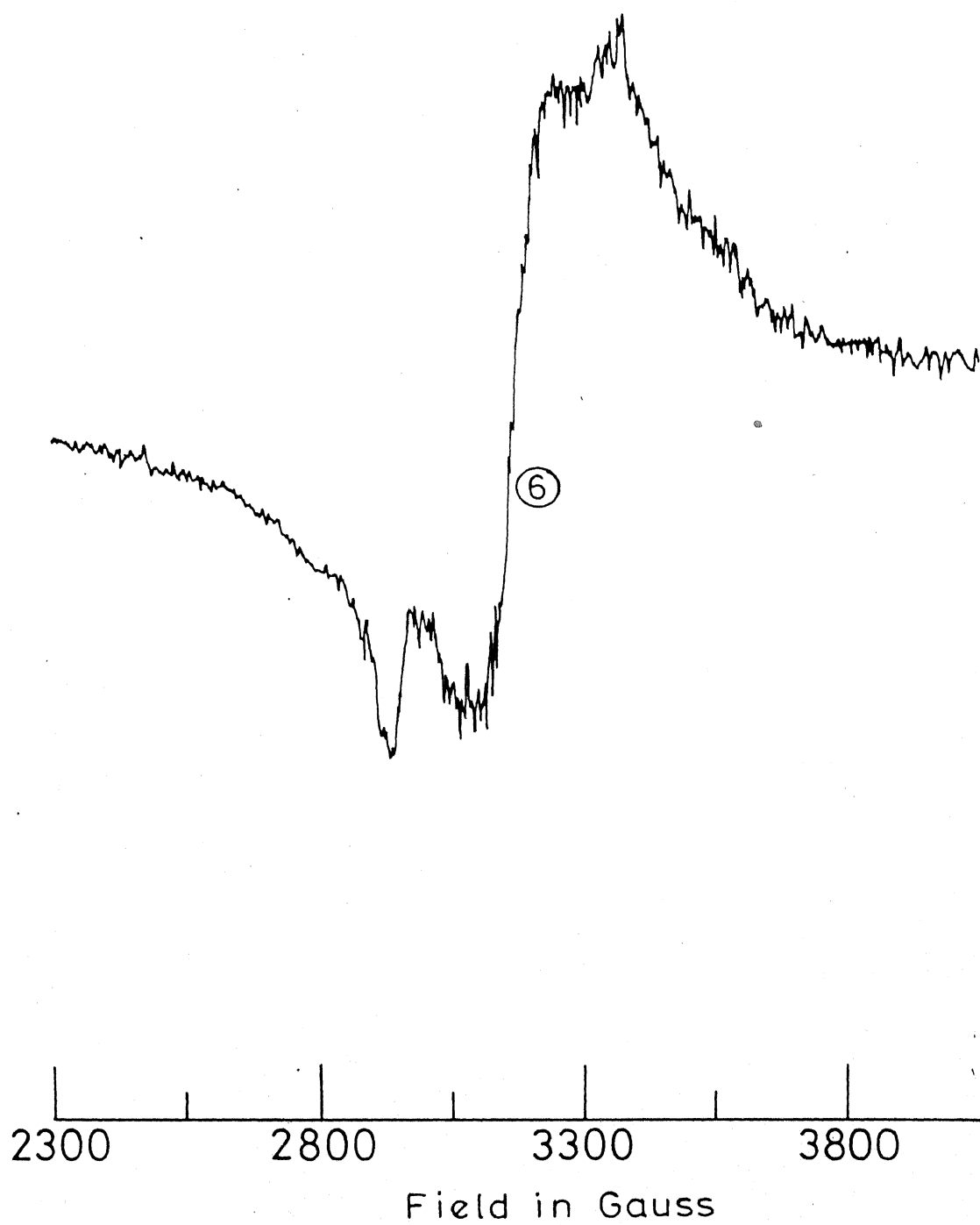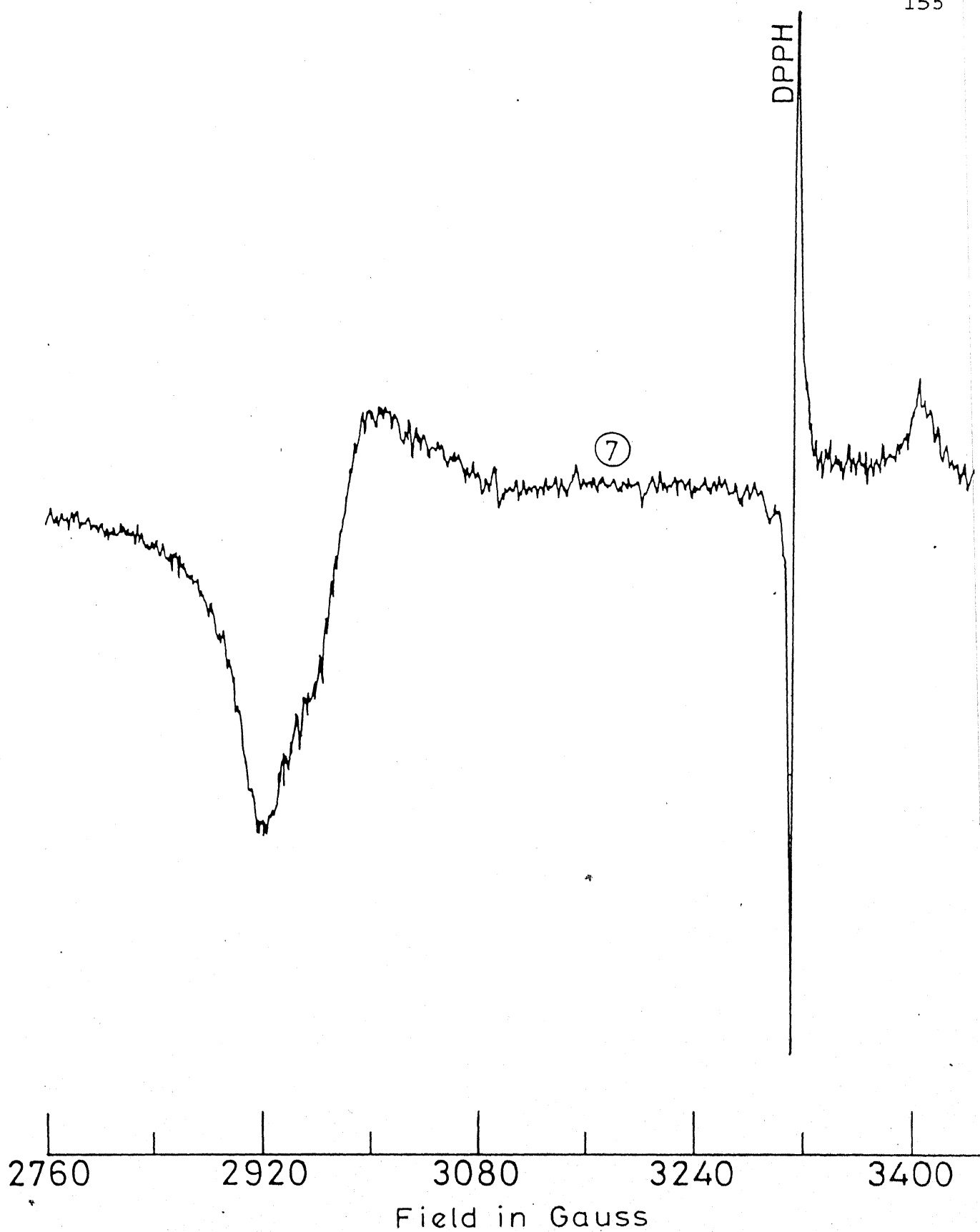
6

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Field in Gauss
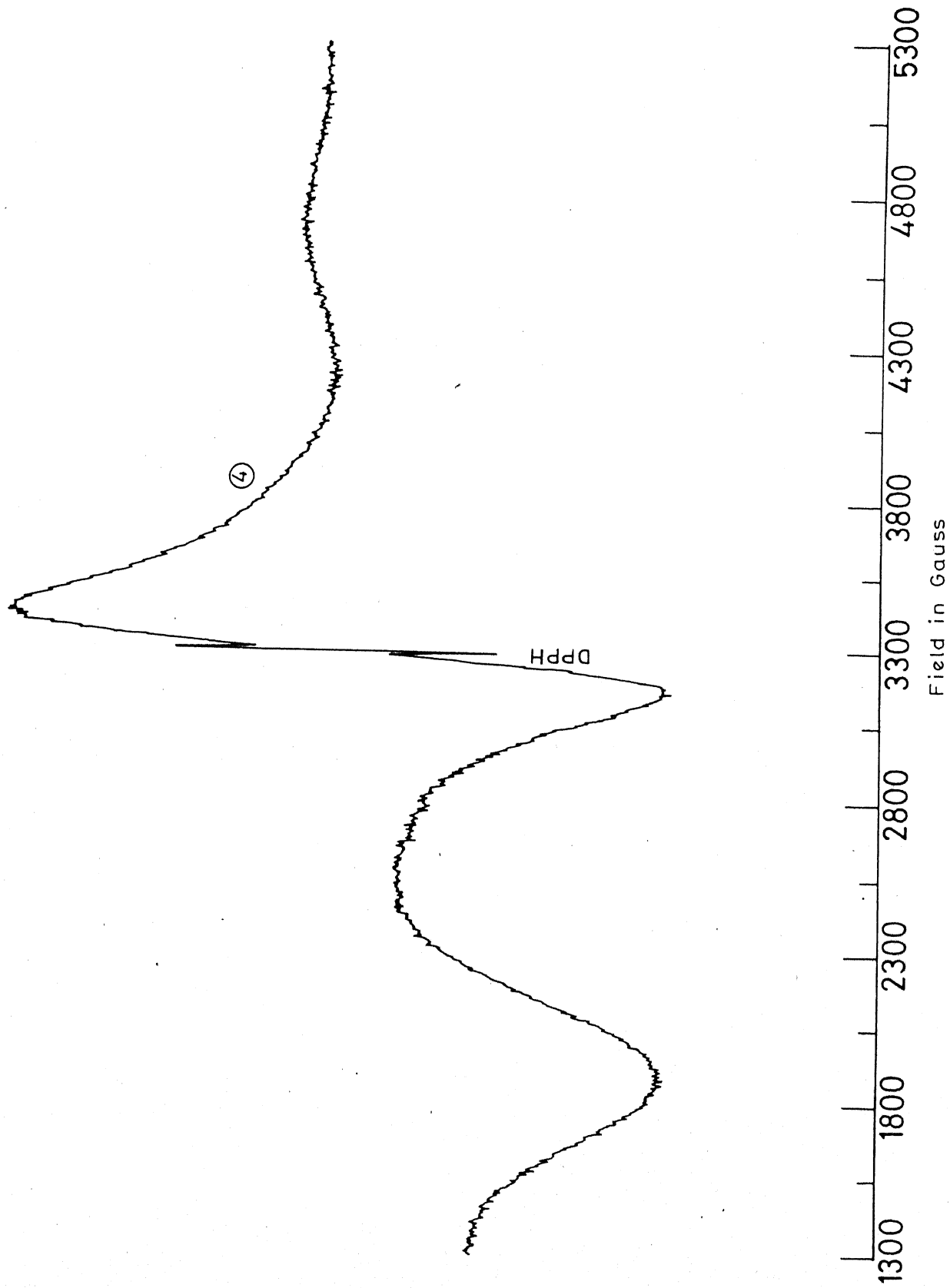
Fig. III.3 ESR spectra

Fig. III.3 ESR spectra

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15. Effective g values are those calculated on the assumption that the resonance occurs between levels described as

belonging to a system with an effective spin (S') of $\frac{1}{2}$, for which $h = g_{eff} H$. The real spin is in this case is $S = 5/2$.

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Chapter IV

TRANSITION METAL COMPLEXES OF N-ETHOXYCARBONYLTHIOPHENE-2-
THIOCARBOXAMIDE: SULPHUR ABSTRACTION FROM N-ETHOXYCARBONYL-
THIOPHENE-2-THIOCARBOXAMIDE BY Ag(I), Cu(II), Pb(II), Hg(II)
AND Cd(II) IONS*

This chapter describes the reactions of N-ethoxycarbonyl-
thiophene-2-thiocarboxamide (ETH) with transition metal ions,
viz., Cu(II), Ni(II), Ag(I), Ru(III), Rh(I), Rh(III), Pd(II) and
Pt(II). These reactions lead to the formation of complexes of
formulae $Cu(ET)_2$, $[Ni(ET)_2Py]$ (in the presence of pyridine),
AgET, $[Ru(ET)_2Cl(H_2O)]$, $[Rh(ETH)(PPh_3)Cl]_2$, $[Rh(ET)_2Cl(H_2O)]$,
$Pd(ET)_2$ and $Pt(ET)_2$, respectively. Reactions of ETH with Ag(I),
Cu(II), Pb(II), Hg(II) and Cd(II) under reflux condition yield
the corresponding sulphides and the oxygenated form of the
ligand. In the reaction of ETH with Ag(I) under reflux condi-
tion, the oxygenated form of the ligand was also isolated, along
with Ag_2S, and characterised as N-ethoxycarbonylthiophene-2-
carboxamide. The complexes, thus obtained, have been characte-
rised on the basis of chemical analyses, conductivity, spectro-

scopic and magnetic measurement studies in order to determine the tentative structures.

IV.1 EXPERIMENTAL

All the chemicals used were of AnalaR or chemically pure grade. The method of analyses and the instruments used were same as described in earlier chapters.

IV.1.1 Preparation of N-Ethoxycarbonylthiophene-2-thiocarbox-amide (ETH)[1]

The first step in the synthesis of ETH involved the pre-paration of ethoxycarbonylisothiocyanate (SCNCOOEt) followed by reaction of thiophene with SCNCOOEt resulting in the forma-tion of N-ethoxycarbonylthiophene-2-thiocarboxamide (ETH).

(i) Preparation of Ethoxycarboxylisothiocyanate (SCNCOOEt)

A mixture of 700 ml of dry acetonitrile and 194 g (2.0 mol) of potassium thiocyanate was warmed on steam bath and treated portionwise with 217 g (2.0 mol) of ethylchloroformate, heating was continued until the reaction mixture became hot and inorga-nic precipitate thickened rapidly. At this point the mixture became yellow. The heat source was removed and reaction allowed to run its course. The mixture was permitted to cool slowly at room temperature, chilled and suction filtered. The filtrate was concentrated under reduced pressure and residual oil distilled,

yield: 162 g, b.p. 51° (at 13 mm). Redistillation at 10 mm showed that bulk of material distilled at 44°C.

(ii) Preparation of N-Ethoxycarbonylthiphene-2-thiocarboxamide (ETH)

A mixture of 8.4 g (0.10 mol) of thiophene, 13.1 g (0.10 mol) of ethoxycarbonylisothiocyanate (SCNCOOEt) and 10 ml of anhydrous stannic chloride ($SnCl_4$) solidified completely when allowed to stand for 4 hr. The reaction flask was cooled occasionally during the early stage of reaction to prevent over heating of reaction mixture. Resulting solid was ground into a powder and thoroughly mixed with dil. HCl. Filtration followed by washing of precipitate first with dil. HCl and then with water, yielded 17.5 g (81%) of the compound ETH. Recrystallisation from CCl_4 yielded the pure compound as dark red crystals, m.p. 107-108°C.

IV.1.2 Preparation of Complexes

(i) Bis(N-ethoxycarbonylthiophene-2-thiocarboxamidato)copper(II)

A cold solution of ETH (0.86 g, 4 mmol) in EtOH (25 ml) was added dropwise to a ice-cold solution of $CuCl_2.2H_2O$ (0.34 g, 2 mmol) in water (25 ml), immediate light green precipitate results. The precipitate was centrifuged, washed with water, alcohol and ether and dried in vacuo.

(ii) Bis(N-ethoxycarbonylthiophene-2-thiocarboxamidato)(pyridine)nickel(II)

A cold solution of ETH (0.86 g, 4 mmol) in ethanol (10 ml) was added dropwise to ice-cold solution of $Ni(NO_3)_2.6H_2O$ (0.64 g, 2.2 mmol) in water (25 ml) containing 5 ml of pyridine. Brown colour nickel complex results. The compound was filtered off then washed with water and dried first under suction and then at $40^{o}C$.

(iii) N-Ethoxycarbonylthiophene-2-thiocarboxamidatosilver(I)

A solution of ETH (0.43 g, 2 mmol) in ethanol (10 ml) was added to a stirred solution of $AgNO_3$ (0.34 g, 2 mmol) in water (10 ml) at room temperature. The resultant yellow precipitate was filtered off, washed with water, alcohol and ether and dried in vacuo. The compound decomposes on heating or on standing for more than a day.

(iv) Aquachlorobis(N-ethoxycarbonylthiophene-2-thiocarboxamidato)ruthenium(III)

A hot solution of $RuCl_3.3H_2O$ (0.26 g, 1 mmol) in ethanol (100 ml) was mixed with the solution of ETH (0.43 g, 2 mmol) in ethanol (20 ml). The resulting mixture was heated under reflux for 3 hr to give violet compound which was centrifuged, washed with alcohol and ether and dried in air. The filtrate was concentrated to about 10 ml on water bath and enough ether was added which resulted in the precipitation of additional violet

complex. The compound was separated and washed with ethanol and ether and dried in vacuo.

(v) Aquachlorobis(N-ethoxycarbonylthiophene-2-thiocarboxamidato)-rhodium(III)

A solution of ETH (0.43 g, 2 mmol) in ethanol (10 ml) was added to stirred solution of $RhCl_3.3H_2O$ (0.26 g, 1 mmol) in water (50 ml). The resulting orange colloidal solution was digested on water bath for 1.5 hr and the orange yellow rhodium complex was then filtered off, washed with water then with small quantity of ethanol and ether and dried in vacuo.

(vi) Di-μ-chlorobis(N-ethoxycarbonylthiophene-2-thiocarboxamide)-bis(triphenylphosphine)dirhodium(I)

A solution of ETH (0.14 g, 0.6 mmol) in dichloromethane (25 ml) was mixed with solution of $\left[RhCl(PPh_3)_3\right]$ (0.46 g, 0.5 mmol) in dichloromethane (25 ml). The resulting mixture was heated under reflux for 15 min. and the solution was then cooled to room temperature and concentrated to 5 ml at reduced pressure. The addition of petroleum ether (40-60°) to this solution caused precipitation of the yellow rhodium complex. The yellow complex was filtered and washed with ether and dried in vacuo.

(vii) Bis(N-ethoxycarbonylthiophene-2-thiocarboxamidato)-palladium(II)

A solution of ETH (0.43 g, 2 mmol) in ethanol (20 ml) was added to hot solution of $PdCl_2.2H_2O$ (0.21 g, 1 mmol) in water

(50 ml), immediate yellow palladium complex appeared. The pre-
cipitate was separated through filtration and washed with water,
alcohol and ether and dried in air.

(viii) Bis(N-ethoxycarbonylthiophene-2-thiocarboxamidato)-
platinum(II)

A solution of ETH (0.43 g, 2 mmol) in ethanol (25 ml) was
added to solution of $PtCl_4.5H_2O$ (0.43 g, 1 mmol) in water (25 ml).
The mixture was heated under reflux for 1 hr. The dark brown
precipitate appeared. The precipitate was separated and washed
with water, alcohol and ether and dried in air.

IV.1.3   Sulphur Abstraction from ETH by Soft Metal Ions

A water solution of hydrated metal salts$^{\neq}$ (approx. 1 mmol)
was mixed with ethanolic solution of ETH (approx. 1.5 mmol). The
mixture was heated under reflux for 2-4 hr. The respective sul-
phides Ag_2S (black), CuS (black), PbS (black), HgS (black) and
CdS (yellow) were precipitated and characterised after separa-
tion. The filtrate obtained from reaction of $AgNO_3$ and ETH was
evaporated to dryness on steam-bath, the resultant (almost colour-
less) residue was crystallised from chloroform. These crystals
were recrystallised from the mixture of carbon tetrachloride and
ethyl acetate (1:1 ratio). The resulting needle shape colourless

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$\neq$ $AgNO_3$, $CuCl_2.2H_2O$, $Pb(NO_3)_2$, $HgCl_2$ or $CdSO_4.4H_2O$.

crystalline compound melts at 139°C (reported m.p. 142°C) and characterised[1] as N-ethoxycarbonylthiophene-2-carboxamide. Abstraction of sulphur by soft metal ions from similar ligands was also reported earlier from our laboratory.[2]

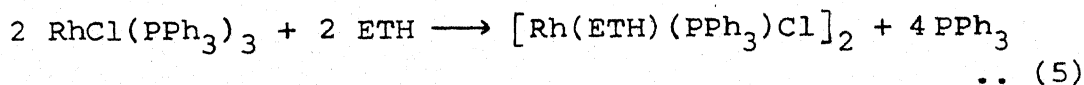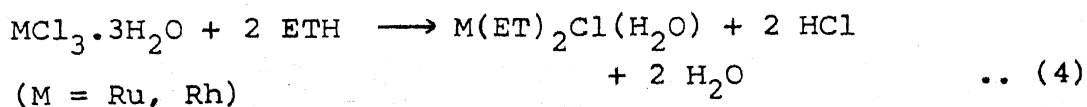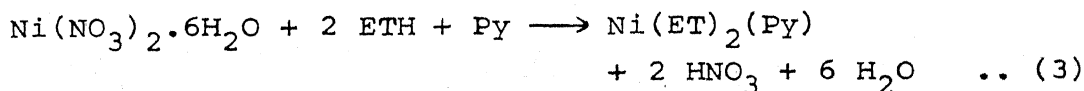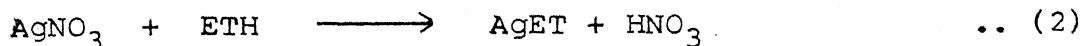## IV.2 RESULTS AND DISCUSSION

IV.2.1 Reactions

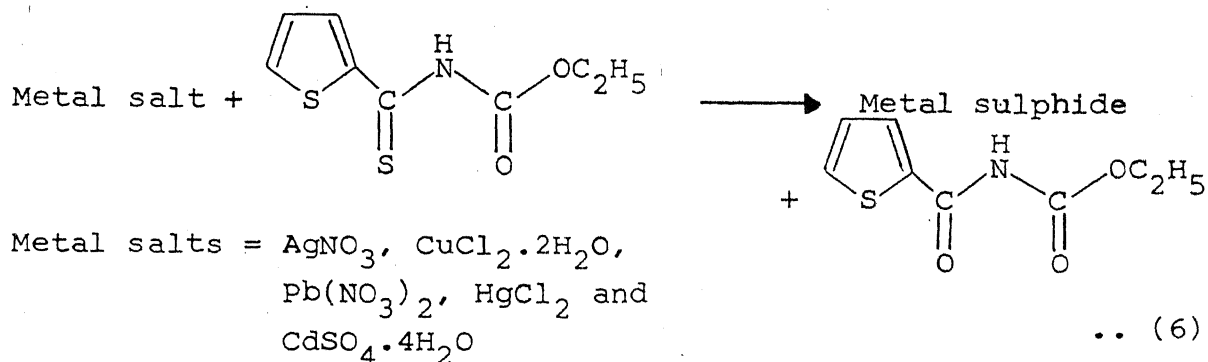The complexation reactions of metal salts with title ligand (ETH) can be described by the following equations:

$$\text{Metal chloride} + 2\ \text{ETH} \longrightarrow \text{M(II)(ET)}_2 + 2\ \text{HCl} \qquad \text{.. (1)}$$
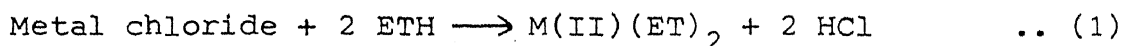
(metal chloride = $CuCl_2 \cdot 2H_2O$, $PdCl_2 \cdot 2H_2O$
and $PtCl_4 \cdot 5H_2O$)

In case of Pt(IV) chloride, ligand first reduces Pt(IV) to Pt(II) and then gives Pt(II)(ET)$_2$. The oxidised form of the ligand does not ligate. Its isolation and characterisation are in progress.

$$\text{AgNO}_3 + \text{ETH} \longrightarrow \text{AgET} + \text{HNO}_3 \qquad \text{.. (2)}$$

$$\text{Ni(NO}_3)_2 \cdot 6H_2O + 2\ \text{ETH} + \text{Py} \longrightarrow \text{Ni(ET)}_2\text{(Py)}$$
$$+ 2\ \text{HNO}_3 + 6\ H_2O \qquad \text{.. (3)}$$

$$\text{MCl}_3 \cdot 3H_2O + 2\ \text{ETH} \longrightarrow \text{M(ET)}_2\text{Cl(H}_2\text{O)} + 2\ \text{HCl}$$
$$+ 2\ H_2O \qquad \text{.. (4)}$$
(M = Ru, Rh)

$$2\ \text{RhCl(PPh}_3)_3 + 2\ \text{ETH} \longrightarrow [\text{Rh(ETH)(PPh}_3\text{)Cl}]_2 + 4\ \text{PPh}_3$$
$$\text{.. (5)}$$

With soft metal ions, on refluxing, instead of complexation, sulphur abstraction takes place, resulting in the formation of metal sulphide and oxygenated form of the ligand according to following equation:

Metal salt + [structure: thiophene ring–C(=S)–N(H)–C(=O)–OC$_2$H$_5$] $\longrightarrow$ Metal sulphide

Metal salts = $AgNO_3$, $CuCl_2 \cdot 2H_2O$, $Pb(NO_3)_2$, $HgCl_2$ and $CdSO_4 \cdot 4H_2O$

+ [structure: thiophene ring–C(=O)–N(H)–C(=O)–OC$_2$H$_5$]

$$\cdots (6)$$

Analytical data (Table IV.1) are in a good agreement with the stoichiometry proposed for complexes. Ru(III), Rh(I) and Rh(III) complexes were found non-conducting in nature.

IV.2.2   IR Spectra

The ligand N-ethoxycarbonylthiophene-2-thiocarboxamide (ETH) contains a thioamide (HNCS) group which gives rise to four characteristic thioamide bands in the region of 1500, 1300, 1000, and 800 cm^{-1}. These thioamide bands namely, I, II, III and IV (Table IV.2) have principal contributions from $(\delta_{C-H} + \delta_{N-H})$, $(\nu_{C=S} + \nu_{C-N} + \delta_{C-H})$, $(\delta_{C-N} + \nu_{C \cdots S})$ and $\nu_{C \cdots S}$ modes of vibration, respectively.[3]

The disappearance of ν(N-H) of ETH from the i.r. spectra of complexes indicates the displacement of the N-H hydrogen by metal ions and formation of metal-nitrogen bond.   Absence of

ν(NH) in the spectrum of $\left[\text{Rh(ETH)(PPh}_3\text{)Cl}\right]_2$ may be attributed to possible coordination of ETH through N and there may be strong hydrogen bonding in solid state of the compound. The broad bands around 3300-3500 cm^{-1} and 1630 cm^{-1} in the spectra of Ru(III) and Rh(III) complexes are tentatively assigned to stretching (anti-symmetric and symmetric) and bending modes of vibration of water molecule.[4]

The ν(C=O) band of the ligand at 1730 cm^{-1} either remains stationary or shifts towards higher wave number in the spectra of all complexes except AgET. This observation rules out the possibility of ligand coordination through carbonyl group. In the spectrum of AgET, ν(C=O) was shifted towards lower wave number by about 65 cm^{-1}, indicating the involvement of carbonyl group in coordination. The ν(C=S) band of the ligand at 1180 cm^{-1} is absent in the spectra of complexes except AgET and Rh(I) complex probably as a result of coordination through thiocarbonyl group, the ν(C=S) either affected to such an extent that practically there is no band at that position or shifted towards lower wave numbers and merged with the band around 1100 cm^{-1} present in most of the spectra of the complexes. In the spectra of AgET and Rh(I) complex ν(C=S) shifted towards higher energy side by 20 cm^{-1} indicating the non-involvement of C=S group in the coordination.

The thioamide band I is relatively weak and/or at little lower energy side in the spectra of complexes except AgET.

The thioamide band II is either relatively weak or splits as a result of coordination. This indicates the possibility of simultaneous coordination through N and S.

The thioamide band III ($\nu_{C-N} + \nu_{C\cdots S}$) shifted towards lower wave number by 10-30 cm^{-1} and is weak (in some cases almost absent) in the spectra of complexes. This may be taken as support for strong and simultaneous involvement of N and S. There is asymmetrical change in the position of band IV after complexation which suggests[5] the simultaneous coordination of ligand through N and S. The two new bands of considerable intensity at 1570 and 1470 (1440 in case of Ni(ET)$_2$Py) cm^{-1} in the spectra of Cu(ET)$_2$ and Ni(ET)$_2$Py may be assigned to ν(C=N) and ν(N-C=S), respectively.[6] All the characteristic bands of pyridine were present with small shift in the spectrum of Ni(ET)$_2$Py.

New bands of weak to medium intensity in the region 250-500 cm^{-1} in the spectra of some of the complexes are tentatively assigned to coupled vibrations of ν(M-Cl), ν(M-N) and ν(M-S).[7]

IV.2.3 Electronic Spectra

The electronic spectrum of ETH in ethanol exhibits two strong transitions at 292 nm and 350 nm which are assigned to $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ intraligand (IL) transitions, respectively because usually n $\rightarrow \pi^*$ transitions involving sulphur and nitrogen are relatively less intense than $\pi \rightarrow \pi^*$ transitions.[8] The spectra of almost all the compounds (Table IV.3) show the

presence of these two bands with the hypsochromic blue shift of 10-20 nm. The high intensity of these bands suggests that they should be charge transfer (CT) or intraligand (IL) and not d-d transition bands. The absence of band around 350 nm (n $\rightarrow \pi$ *) from the spectra of copper and platinum complexes may be due to stabilization of the energy of the lone pairs of electron on complex formation[9] and similarly the hypsochromic shift in ($\pi \rightarrow \pi$ * and n $\rightarrow \pi$ *) bands in the spectra of complexes may be explained as metal ions are bonded to thiocarbonyl sulphur and nitrogen,[10] these bonds formation lower the energy of non-bonding orbitals as well as π-levels, thus now more energy will be required to promote the electron from n or π level to π * orbital hence the observed hypsochromic shift.

The weak shoulder at 410 nm (in Pd complex) and 460 nm (in Pt complex) is assigned to a d-d, $d_{x^2-y^2} \rightarrow d_{xy}$ ($^1A_{1g} \rightarrow {}^1B_{1g}$) transition for square-planar complexes. The most of the expected d-d transitions were probably masked by strong CT and/or IL transitions. Weak shoulder at 430 nm in the spectrum of $[Ru(ET)_2Cl-(H_2O)]$ complex could be assigned to $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$ transition.[11]

IV.2.4 Magnetic Properties

All compounds except Ni(II) and Ru(III) complexes were found diamagnetic at room temperature. The magnetic moments of Ni(II) and Ru(III) complexes correspond to two and one unpaired electron(s), respectively (Table IV.1).

Thus, on the basis of analytical, spectral and magnetic measurement data, the following tentative geometries have been assigned to the complexes.

$CuET_2$, $PdET_2$ and $PtET_2$ — Square planar

$[Ru(ET)_2Cl(H_2O)$ and $)$
$[Ru(ET)_2Cl(H_2O)$ $)$ — Octahedral
$)$

$Ni(ET)_2Py$ — Square pyramidal

$[Rh(ETH)(PPh_3)Cl]_2$ — Square planar (dimeric)[12]

AgET — Linear
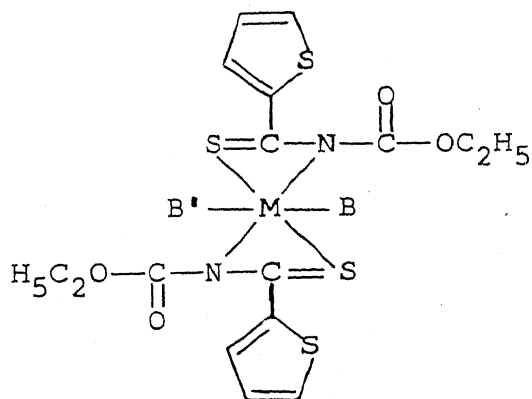
M = Cu, Pd or Pt; B,B' = nil
M = Ru, Rh(III); B = Cl, B' = H_2O
M = Ni; B = Py; B' = nil

$[Rh(ETH)(PPh_3)Cl]_2$

AgET
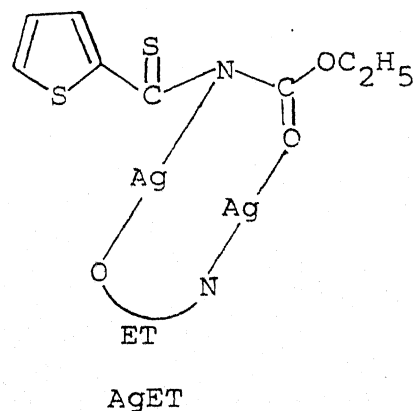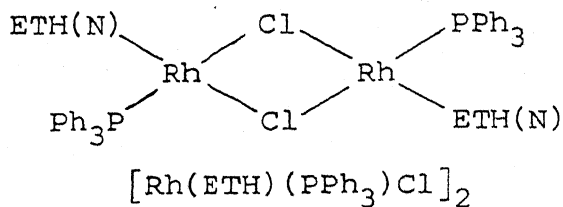
Table IV.1. Analytical and Magnetic Data

| | Colour | m.p. (°C) | Analyses: Found (Calcd.), % | | | | | | μ_{eff} (B.M.) | Yield (%) |
			M	S	C	H	N	Cl		
Cu(ET)$_2$	Light green	90d	12.7 (12.9)	26.1 (26.0)	38.9 (39.1)	3.2 (3.3)	5.7 (5.7)	–	DM	55
Ni(ET)$_2$(Py)	Brown	45	10.3 (10.4)	22.5 (22.6)	44.7 (44.5)	3.6 (3.7)	7.3 (7.4)	–	3.14	50
AgET	Yellow	152d	33.4 (33.5)	20.0 (19.9)	29.7 (29.8)	2.5 (2.5)	4.4 (4.3)	–	DM	80
[Ru(ET)$_2$Cl(H$_2$O)]	Violet	240	17.4 (17.3)	22.1 (22.0)	32.9 (33.0)	3.0 (3.1)	4.9 (4.8)	6.2 (6.1)	2.06	50
[Rh(ETH)(PPh$_3$)Cl]$_2$[a]	Yellow	115	– (16.7)	10.4 (10.4)	50.8 (50.7)	4.0 (3.9)	2.4 (2.3)	5.9 (5.8)	DM	70
[Rh(ET)$_2$Cl(H$_2$O)]	Orange yellow	175d	– (17.6)	21.7 (21.9)	33.0 (32.8)	3.2 (3.1)	4.7 (4.8)	6.0 (6.1)	DM	60
Pd(ET)$_2$	Orange yellow	83	20.0 (19.9)	24.1 (24.0)	36.1 (35.9)	3.0 (3.0)	5.4 (5.2)	–	DM	65
Pt(ET)$_2$	Dark brown	240	31.1 (31.3)	20.6 (20.5)	31.0 (30.8)	2.5 (2.6)	4.6 (4.5)	–	DM	45

At 293 K and uncorrected for diamagnetism, DM = diamagnetic, d = decomposes

a, P = 4.8 (5.0).

Table IV.2. Major IR Bands of Interest. Comparison of IR Spectra of Complexes with Ligands

Compound	ν(OH)	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands				Possible coordination through
					I	II	III	IV	
Ligand ETH	-	3240s,br	1730s	1180s	1510–1530s,br	1360s	1020s	770s	-
Cu(ET)$_2$	-	-	1730m	-	1510m	1360m, 1380m	995m	790s	N and S
AgET	-	-	1650–1680m,br	1200s	1550m,br	1350m, 1370m	990w, 1040s	790w	N and O
Ni(ET)$_2$(Py)	-	-	1750w	-	1510m	1350m, 1370m	1010w	760w	N and S
[Ru(ET)$_2$Cl(H$_2$O)]	3460br, 1630m,br	-	1730m	-	1520m	1360s	-	780m	N and S
[Rh(ETH)(PPh$_3$)Cl]$_2$	-	-	1730m	1200m	1520w	1360w	-	760m	N
[Rh(ET)$_2$Cl(H$_2$O)]	3380br 1630w	-	1760m,br	-	1520m	1360s	1010m	-	N and S
Pd(ET)$_2$	-	-	1730m	-	1520m	1360s 1380s	1010m	775w, 800s	N and S
Pt(ET)$_2$	-	-	1740m,br	-	1500m,br	1370w	1010w	750s	N and S

Table IV.3. Electronic Spectra of the Ligand and Complexes
in 95% Ethanol

Compound	Band position λ_{max} (nm)	Assignment
Ligand ETH	292	$\pi \longrightarrow \pi^*$
	350	$n \longrightarrow \pi^*$
$Cu(ET)_2$	280	IL
$Ni(ET)_2(Py)$	280	IL
	330	IL
AgET	285	IL
	340sh	IL
$[Ru(ET)_2Cl(H_2O)]$	260	CT or IL
	330sh	IL
	430w,sh	$^2T_{2g} \longrightarrow {}^2A_{2g}, {}^2T_{1g}$
$[Rh(ETH)(PPh_3)Cl]_2$	280vw,sh	IL
	325vw,sh	IL
$[Rh(ET)_2Cl(H_2O)]$	280w,sh	IL
	330	IL
$Pd(ET)_2$	255	CT
	285w	IL
	330	IL
	410w,sh	d-d
$Pt(ET)_2$	295w	IL
	460w,br,sh	d-d

sh = shoulder; vw = very weak, br = broad.

LEGEND TO FIGURES

Fig. IV.1   Infrared Spectra

    1. ETH

    2. $Ni(Et)_2(py)$

    3. AgEt

    4. $Rh(Et)_2Cl.H_2O$

    5. $Cu(Et)_2$

    6. $[RhCl(PPh_3)(ETH)]_2$

Fig. IV.2   Electronic Spectra (in Ethanol)

    1. ETH

    2. $Cu(Et)_2$

    3. AgEt

    4. $Rh(Et)_2Cl.H_2O$

    5. $Pt(Et)_2$

    6. $Ni(Et)_2(py)$

    7. $Pd(Et)_2$
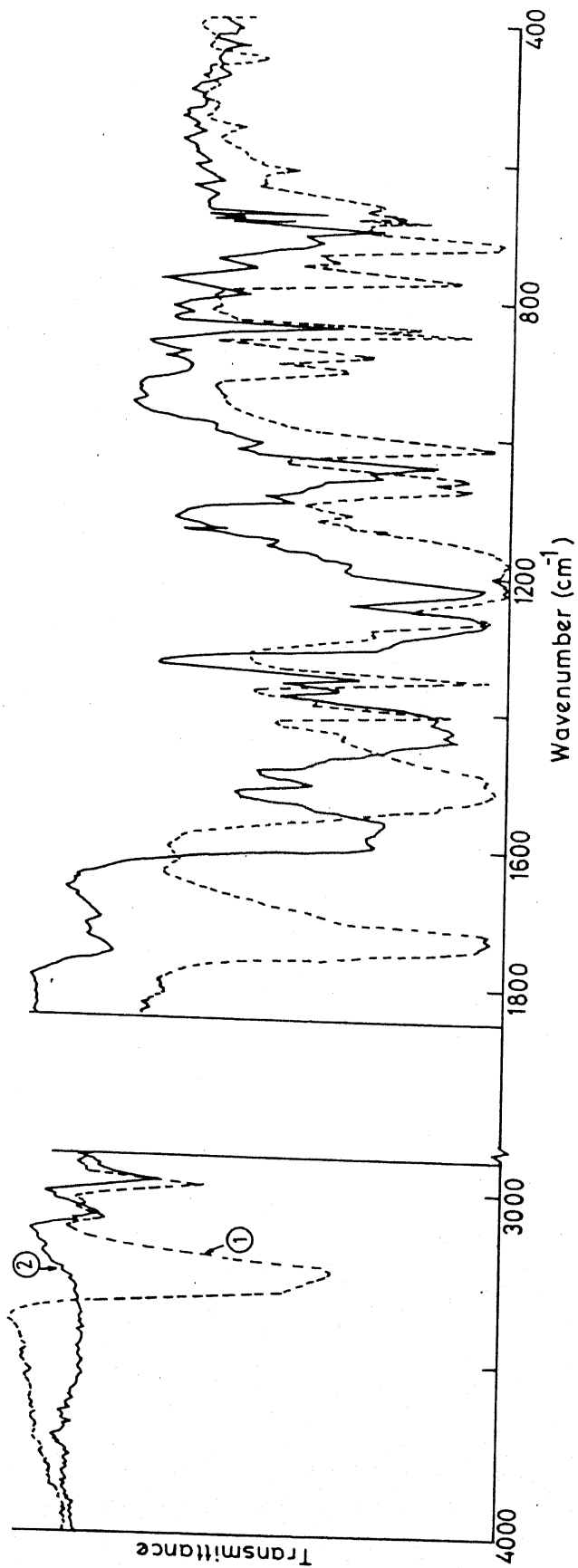
Fig.IV.1 IR Spectra
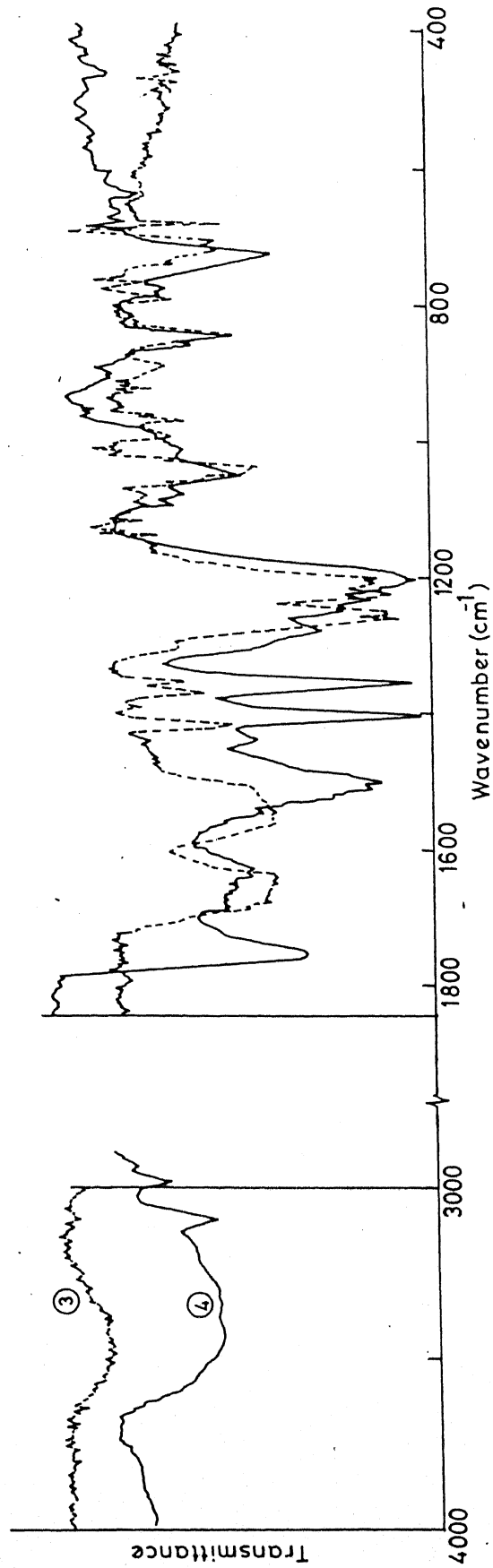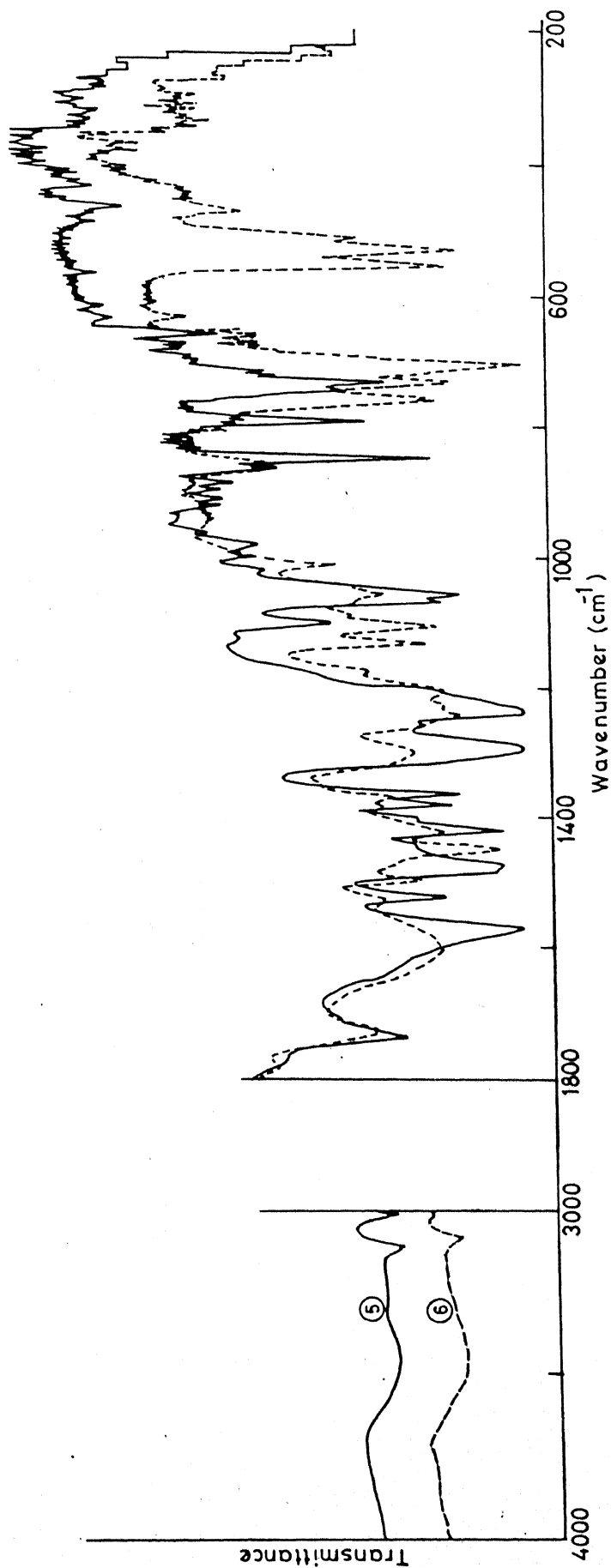
Fig. IV·1 IR Spectra

Fig.IV·1 IR Spectra
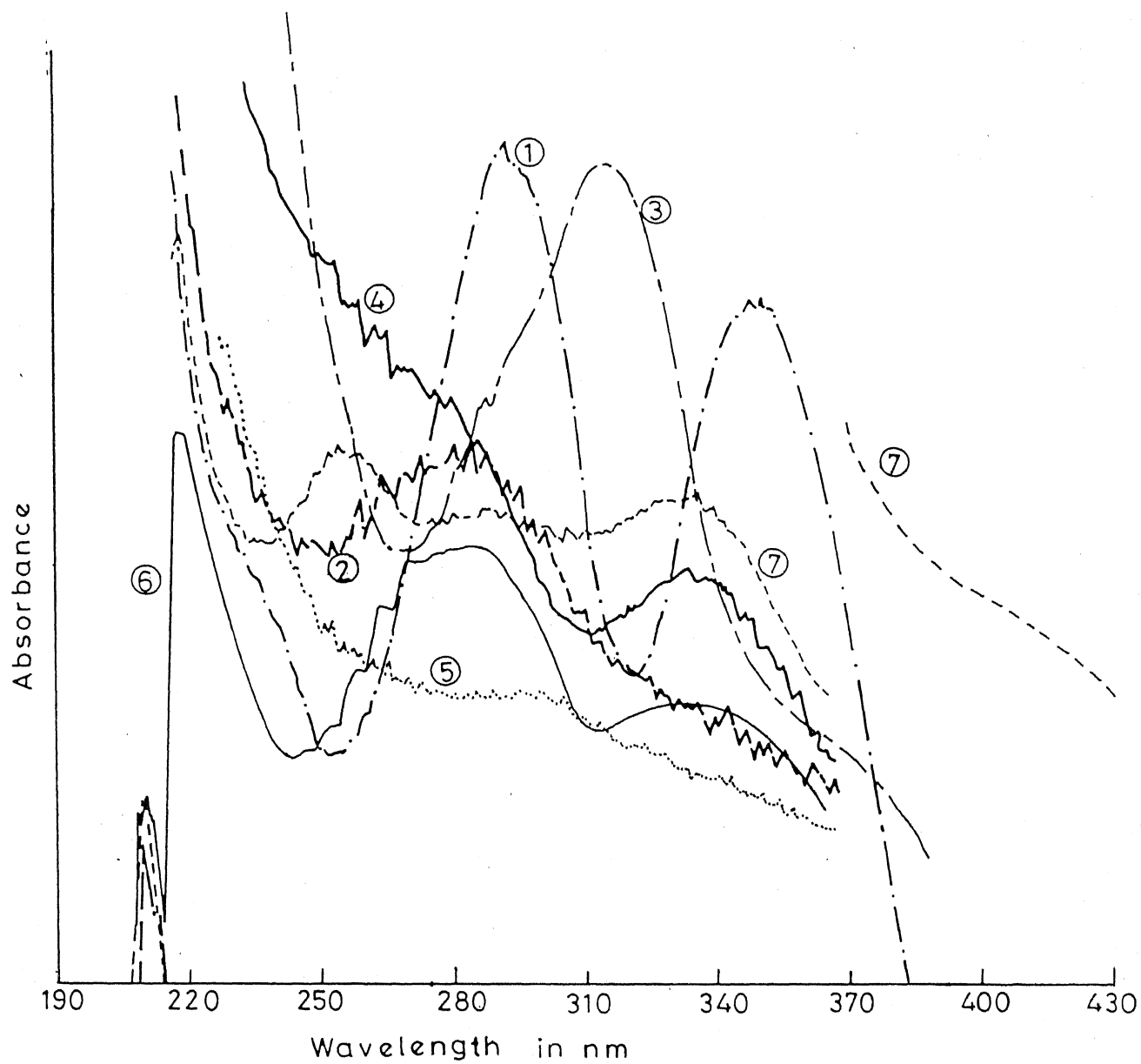
Fig. IV.2 Electronic spectra

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Chapter V

REACTIONS OF $[RuCl_3(AsPh_3)_2(CH_3OH)]$ AND $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ WITH SOME THIO-CARBOXA(I)MIDES: SYNTHESES & CHARACTERI-SATION OF RUTHENIUM(II) THIOCARBOXA(I)MIDE COMPLEXES

This chapter describes the reactions of $[RuCl_3(AsPh_3)_2(CH_3OH)]$ and $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ with thiocarboxamides of the type $RCSNHCOOC_2H_5$ (R = 2-pyrrole, 2-thiophene or 4-toluene), $RCSNHCONHC_6H_5$ (R = 2-pyrrole) and 2-thiopyrrole-1,2-dicarboximide. The reactions of $[RuCl_3(AsPh_3)_2(CH_3OH)]$ with these ligands led to formation of the diamagnetic complexes $[RuCl_2(AsPh_3)(ligand)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$ and $[RuCl_2(AsPh_3)(ligand)_2]_2$ (in case of ligand $RCSNHCONHC_6H_5$ (R = 2-pyrrole)) in absence of CH_2Cl_2 in the medium. The reactions of these ligands with $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ afford the diamagnetic magnetic complexes $[(\eta^5-C_5H_5)RuCl(PPh_3)(ligand)]$ by the substitution of one triphenylphosphine by a ligand molecule. The products thus obtained were characterised by means of chemical analyses, conductance, magnetic measurements,

molecular weight determinations and spectroscopic (IR, UV, Visibl

and proton NMR) studies. Their probable structures have been

suggested.

V.1 EXPERIMENTAL

All the chemicals used were either of AnalaR or chemically

pure grade. Solvents were dried before use and all the reactions

were carried out under dry N_2 atmosphere. The methods of elemen-

tal analyses, recording of IR spectra, melting points and magnetic

measurements have been described in previous Chapters II & III.

The electronic spectra were recorded on Shimadzu double beam

spectrophotometer UV-190. The proton NMR spectra were recorded

on a Varian's EM-390 90 MHz spectrometer in the range δ0-20 ppm

in $CDCl_3$ using tetramethylsilane (TMS, $\delta = 0$) as calibrant. The

conductivity measurements of the complexes were made on an Elico

conductivity meter type CM-80. The molecular weights were deter-

mined by elevation of boiling point and/or depression of freezing

point method. The ligands and starting compounds $[RuCl_3(AsPh_3)_2-$

$(CH_3OH)]$ and $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ were prepared by following

literature methods.

V.1.1 Preparation of Ligands[1]

(i) Ethoxycarbonylisothiocyanate (SCNCOOEt)

Its method of preparation has been described in Chapter IV.

(ii) <u>N-Ethoxycarbonylpyrrole-2-thiocarboxamide (EPH)</u>

A mixture of 16.8 g (0.25 mol) of pyrrole and 32.8 g
(0.25 mol) of ethoxycarbonylisothiocyanate, both ice cold, was
swirled occasionally and cooled as needed to prevent its tempe-
rature from rising above 40°C. Within about an hour the mixture
had solidified, whereupon it was allowed to stand overnight.
Following repeated washing of the product with petroleum ether
(b.p. 60-80°C), there was obtained 46 g (93%) of N-ethoxycarbo-
nylpyrrole-2-thiocarboxamide, m.p. 95-98°C. Recrystallisation
of the product from aqueous ethanol gave the pure compound in
the form of yellow crystals, m.p. 98-99°C.

(iii) <u>2-Thiopyrrole-1,2-dicarboximide (TPH)</u>

A mixture of 5.0 g of EPH and 15 ml of quinoline was heated
in a 25 ml erlenmeyer flask until the temperature of the escap-
ing vapours reached 170-180°C. The resulting tarry material was
cooled, subsequently mixed with cold dilute hydrochloric acid
and extracted with ether. The ether extract was washed with water,
treated with charcoal and dried over $MgSO_4$, finally it was evapo-
rated to dryness to yield 3.3 g (87%) of TPH, m.p. 135-138°C.
Recrystallisation from aqueous ethanol gave the product in the
form of orange crystals, m.p. 140-141°C.

(iv) <u>N-Ethoxycarbonylthiophene-2-thiocarboxamide (ETH)</u>

Its method of preparation has been described in Chapter IV.

(v) <u>N-Phenylcarbamoylpyrrole-2-thiocarboxamide (PPH)</u>

A mixture of 1.0 g of N-ethoxycarbonylpyrrole-2-thiocarbox-
amide (EPH) and 5 ml of aniline was boiled for about one minute
and resulting solution was cooled and then filtered. Following
washing of precipitate with CCl_4, there was obtained 1.1 g (92%)
of PPH. Recrystallisation from ethanol yielded the pure compound
in the form of yellow crystals, m.p. 213-214°C.

(vi) <u>N-Ethoxycarbonyltoluene-4-thiocarboxamide (ETOLH)</u>

This ligand was prepared in N_2 atmosphere. To a stirred
cold (ice bath) solution of 0.050 mol (4.6 g, 5.4 ml) of toluene
and 6.5 g (0.050 mol) of ethoxycarbonylisothiocyanate in 30 ml of
CH_2Cl_2 was added 13.3 g (0.10 mol) of anhydrous $AlCl_3$ in small
portions (15-20 min.) at 0-3°C. The reaction mixture was stirred
at this temperature for 4 hr and then it was hydrolysed by careful
addition of ice and dilute HCl. Enough CH_2Cl_2 was added to dissol
any solid organic material and the resulting solution was extract-
ed with four 50 ml portion of 10% aqueous NaOH. This extract was
washed with ethyl ether and acidified with conc. HCl (ice bath)
to yield an oil which solidified upon cooling. The solid material
was washed successively with dil. HCl, and H_2O, dried and washed
again with pet. ether (30-60°C) or cold ethyl ether or cold aqueou
ethanol. Purification of the crude product was accomplished by
recrystallisation from pet. ether (30-60° or 60-70° boiling range)
benzene-pet.ether (b.p. 60-75°), cyclohexane or aqueous ethanol.

V.1.2 Preparation of Starting Compounds

(i) Preparation of Trichlorobis(triphenylarsine)methanol-ruthenium(III), $[RuCl_3(AsPh_3)_2(CH_3OH)]$[2]

$RuCl_3 \cdot 3H_2O$ (0.2 g) and six-fold excess of triphenyl-arsine (1.5 g) was refluxed in methanol (after filtration). Within two hours, green crystals of the complex were deposited, which were washed with ether and air dried (70% yield).

(ii) Preparation of Chloro(η^5-cyclopentadienyl)bis(triphenyl-phosphine)ruthenium(II), $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$[3]

This reaction was done under N_2 atmosphere. A filtered solution of $RuCl_3 \cdot 3H_2O$ (0.52, 2 mmol) in dry ethanol (20 ml) was added to rapidly stirred solution of triphenylphosphine (2.10 g, 8 mmol) in refluxing ethanol (100 ml), followed immediately afterward by a solution of freshly distilled cyclopentadiene (1-2 ml) in ethanol (20 ml). The mixture was then refluxed with stirring, until the colour changes from dark brown to orange was completed (45-60 min.) and then cooled in refrigerator overnight. The orange crystalline product which separated, was filtered, washed with cold ethanol (2 x 10 ml), water (2 x 10 ml), ethanol (2 x 10 ml) and light petroleum ether (2 x 10 ml, 40-60°C) and dried to give pure $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$, (1.25 g, 86%), m.p. 131-135°C.

V.1.3 Preparation of Complexes

(i) Preparation of the Complexes $[RuCl_2(AsPh_3)(LH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$ (LH = EPH, ETH, TPH or ETOLH)

50 ml of chloroform solution containing 0.213 g of

$[RuCl_3(AsPh_3)_2(CH_3OH)]$ (0.25 mmol) and 0.75 mmol of appropriate ligand was stirred under N_2 for 4-5 hr. The resulting solution was concentrated upto almost dryness under reduced pressure, the residue was dissolved in minimum quantity of dichloromethane, followed by an addition of excess ($\smile$100 ml) petroleum ether (60-80°) with constant stirring. On standing for 1-2 hr, the precipitate settled down. It was centrifuged, washed several times with pet. ether (60-80°) and dried in vacuo.

(ii) Preparation of Complex $[RuCl_2(AsPh_3)(PPH)_2]_2$

50 ml of chloroform solution containing 0.213 g of $[RuCl_3(AsPh_3)_2(CH_3OH)]$ (0.25 mmol) and 0.186 g (0.75 mmol) of PPH was stirred under N_2. The resulting solution was concentrated upto about 5 ml under reduced pressure, followed by addition of excess pet. ether (60-80°), gave the complex, which was centrifuged, washed several times with pet. ether and dried in vacuo.

(iii) Preparation of the Complexes $[(\eta^5-C_5H_5)RuCl(PPh_3)(LH)]$,
(LH = EPH, ETH, ETOLH, PPH or TPH)

In about 40 ml of methanol solution containing $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$ (0.181 g, 0.25 mmol), 25 ml methanol solution of appropriate ligand (0.35 mmol) was added under N_2. The resulting mixture was refluxed for 3-4 hr. The resulting solution was filtered if needed, then almost dried at reduced pressure, the residue was dissolved in minimum quantity of CH_2Cl_2 followed by an addition of excess pet. ether (60-80°). On scratching the

walls of beaker and allowing to stand for 1-2 hr, the precipitate appears. It was centrifuged, washed several times with pet.ether ($60-80^{\circ}$) and dried _in vacuo_. The yield was in the range 50-60% for all the complexes.

V.1.4 Estimation of Phosphorus[4]

Samples were decomposed with a fusing mixture (Na_2O_2, sugar and $NaNO_3$ in the ratio 20:1:3 in a parr-bomb). The melt was extracted with water and heated to SO_3 fumes after adding concentrated H_2SO_4. It was diluted with water and filtered if necessary. In the filtrate phosphorous was estimated as ammonium phosphomolybdate.

V.2 RESULTS AND DISCUSSION

V.2.1 $\left[RuCl_2(AsPh_3)(LH)_2\right]_2 \cdot \frac{1}{2}CH_2Cl_2$ (LH = EPH, ETH, TPH or ETOLH) and $\left[RuCl_2(AsPh_3)(PPH)_2\right]_2$

Analytical data are consistent with the stoichiometry proposed for the complexes (Table V.1). Conductivity measurements show that they are nonionic in nature. The molecular weights determinations indicate the dimeric nature of the complexes. All complexes were found diamagnetic, indicating +2 oxidation state of ruthenium. Diamagnetic nature of the complexes was also confirmed by x-band ESR studies, as no signal appeared at room temperature whereas under same conditions parent compound $\left[RuCl_3(AsPh_3)_2(CH_3OH)\right]$

showed strong signals.

V.2.1.1 IR and ^{1}H NMR Spectra

The mode of bonding of ligands was decided on the basis
of shifts (Table V.3) in the position of ν(NH), ν(C=O), ν(C=S)
and four thioamide bands after complexation. In all the cases
ν(C=O) of the ligand shifted towards higher wave number in the
i.r. spectrum of the respective complexes, ruling out the possi-
bility of involvement of C=O group in coordination to metal atom.
The thioamide bands II and III have major contribution from
ν(C=N) + ν(C=S) + δ(C-H) and ν(C-N) + ν(C-s), respectively,[5] it
is difficult to ascertain the possibility of coordination through
N or S by inspecting the shifts of these bands as both have con-
tribution from ν(CN) and ν(CS) vibrations. Thioamide band I and
IV having principal contribution[6] from δ(N-H) + ν(C-N) and ν(C⋯S),
respectively, can be used more reliably for deciding the bonding
site. In case of bonding through thiocarbonyl sulphur, the thio-
amide band I, as expected, shifts to higher wave number, band IV
and ν(C=S) shift to lower wave number and in those cases where
the band I shifts to lower wave number, band IV and ν(C=S) either
remain stationary or shift to slightly higher wave number, the
coordination of ligand through its N atom is more likely. The
coordination through ring nitrogen or sulphur of pyrrole or thio-
phene is unlikely as they are weakly basic. The ν(NH) in some of
the complexes becomes too broad and weak to be observable. However,
the NH proton resonance in case of complex with ETOLH was observed

at δ 11.0 whereas it could not be observed for other complexes. The NMR spectra of the complexes showed the proton resonance of dichloromethane at δ 5.3-5.4 and all the characteristic signals of concerned ligands (Table V.5).

All the characteristic bands[7] of triphenylarsine (AsPh$_3$) of the parent compound [RuCl$_3$(AsPh$_3$)$_2$(CH$_3$OH)] were present in the spectra of all complexes. The band at 485(+5) cm^{-1} present in the complexes is assigned to ν(Ru-As). The medium intensity band at 280-290 cm^{-1} may be assigned to ν(Ru-Cl-Ru). The medium intensity bands present in the region 330-450 cm^{-1} may be due to coupled vibrations of terminal ν(Ru-Cl), ν(Ru-S) and ν(Ru-N).[8]

V.2.1.2 Electronic Spectra

The electronic spectra of ligands and complexes were taken in CHCl$_3$, the bands positions and their assignments are given in Table V.5.

The ground state of ruthenium(II) in octahedral complexes is $^1A_{1g}$ and the excited states are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Therefore, one would expect four transition bands due to transitions from $^1A_{1g}$ to $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ but as transitions $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^3T_{2g}$ are spin forbidden (singlet → triplet), they are too weak to be observed. In our case the electronic spectra of the complexes showed continuous absorption in the visible region, therefore, some of d-d transitions were probably masked by this continuous absorption or by charge transfer (CT) or intraligand (IL) bands. However, the presence of shoulder/

band in the region 440-480 nm and 515-555 nm are tentatively assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$, respectively as given in Table V.5. The electronic spectra of ligands EPH, PPH and TPH were taken from the literature[9-11] and on same grounds the spectra of ETH and ETOLH were interpreted.

V.2.2 $[(\eta^5-C_5H_5)RuCl(PPh_3(LH)]$ (LH = EPH, ETH, ETOLH, PPH or TPH

Analytical data are in good agreement with the stoichiometry proposed for the complexes (Table V.2). All compounds were found diamagnetic and non-ionic in nature. The compounds are, in general, air stable and soluble in most of the organic solvents.

V.2.2.1 IR and ^{1}H NMR Spectra

The donor ability of this class of ligands can perhaps be best understood in terms of resonance structures given below:

I II III
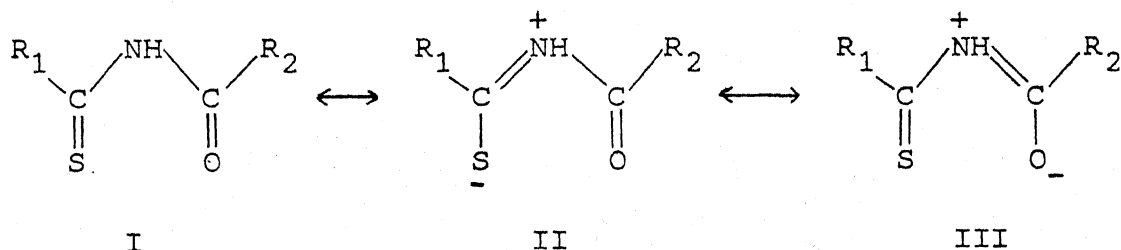
Ordinarily, only structure I is considered but II and III are also quite valid and may predominate under certain situations. In case of coordination of the ligand through its thiocarbonyl sulphur atom the ν(C=S), thioamide band IV ($\nu_{C \cdots S}$) should shift

to lower wave number and thioamide band I $(\delta_{N-H} + \nu_{C-N})$[6] should shift to higher wave number whereas if coordination is through N atom, the thioamide band I will shift to lower wave number. Based on the above criterion bonding mode has been arrived at Table V.4. In all cases the $\nu(C=O)$ of the ligands goes to higher wave number after complexation (Table V.4), hence the coordination through oxygen is ruled out. The coordination through ring nitrogen or sulphur of pyrrole or thiophene is unlikely as they are weakly basic. The thioamide bands II $(\nu_{C \doteq N} + \nu_{C=S} + \delta_{C-H})$ and III $(\nu_{C-N} + \nu_{C-S})$[5] do not shift systematically after complexation hence could not be used reliably for deciding bonding site. The $\nu(NH)$ in some of the complexes could not be observed. All the characteristics bands of PPh_3 and $\eta^5-C_5H_5$ (820-850 cm^{-1})[12,13] were present in the i.r. spectra of the complexes. The new bands of medium intensity in region of 350-480 cm^{-1} may be attributed to coupled vibration of $\nu(Ru-Cl)$, $\nu(Ru-S)$ or $\nu(Ru-N)$.[8]

The proton n.m.r. spectra (Table V.6) of the complexes display a sharp singlet δ 4.1-4.3 (for $\eta^5-C_5H_5$) apart from all characteristic signals of concerned ligands and PPh_3.[1] However, the NH proton resonance could not be detected in the NMR spectra of the complexes.

V.2.2.2 Electronic Spectra

The electronic spectra of the complexes as well as ligands were taken in chloroform. The bands position and their assignments are given in Table V.6. The ground state of ruthenium(II)

in octahedral environment is $^1A_{1g}$ and only two spin allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$, are expected. The band in the region 465-485 nm may be assigned to $^1A_{1g} \rightarrow {}^1T_{2g}$ and a shoulder at 525 nm in ETH complex may be due to $^1A_{1g} \rightarrow {}^1T_{1g}$. Some of the intraligand (IL) bands were present in electronic spectra of respective complexes with small shifts. The intense bands at 240-245 nm and 270-280 nm are assigned to charge transfer CT) transitions.

The diamagnetism of Ru(II), d^6-systems indicate the spin-pairing, hence distorted octahedral structure,[13] assuming that η^5-C_5H_5 group occupies three coordination sites, is preferred over tetrahedral or distorted tetrahedral as spin pairing is not possible in later cases. Thus, on the basis of analytical, spectral (i.r., u.v., visible and ^{1}H n.m.r.) and magnetic moments data, the following structures are proposed for the complexes:

(A)
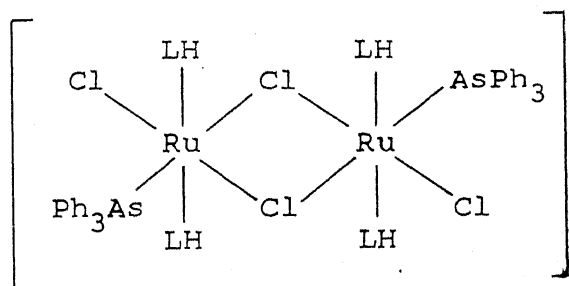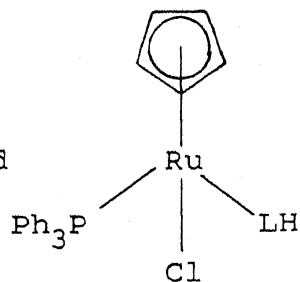
(B)

(Distorted octahedron)

(LH = EPH, ETH, ETOLH, PPH or TPH)

Table V.1. Analytical data of the complexes

Compound	Colour	M.P.	Analyses: Found (Calcd.), %					
			Ru	S	Cl	C	H	N
$[RuCl_2(AsPh_3)(EPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	Brown	>230d	11.0 (11.3)	7.2 (7.1)	10.0 (9.9)	46.1 (45.9)	3.8 (4.0)	6.1 (6.2)
$[RuCl_2(AsPh_3)(ETH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	Bluish violet	88	10.8 (10.9)	13.8 (13.8)	9.7 (9.6)	44.4 (44.2)	3.5 (3.6)	3.1 (3.0)
$[RuCl_2(AsPh_3)(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	Dark maroon	52	10.8 (10.7)	6.7 (6.8)	9.6 (9.4)	50.8 (51.1)	4.3 (4.4)	3.2 (3.0)
$[RuCl_2(AsPh_3)(PPH)_2]_2$	Reddish violet	140d	10.5 (10.4)	6.4 (6.6)	7.1 (7.3)	52.4 (52.1)	3.7 (3.8)	8.8 (8.7)
$[RuCl_2(AsPh_3)(TPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	Bluish violet	>230d	12.3 (12.6)	8.2 (8.0)	10.8 (11.1)	45.5 (45.2)	3.0 (2.9)	6.8 (7.0)

d, decomposes; melting points are uncorrected.

Table V.2. Analytical data of the complexes $[(\eta^5-C_5H_5)RuCl(PPh_3)(ligand)]$

Compound with the ligand	Colour	M.P.	Analyses: Found (Calcd.), %						
			Ru	S	Cl	C	H	N	P
EPH	Red	82	15.6 (15.3)	5.0 (4.8)	5.3 (5.4)	56.0 (56.2)	4.4 (4.5)	4.3 (4.2)	4.5 (4.7)
ETH	Reddish violet	84d	15.0 (14.9)	9.3 (9.4)	5.4 (5.2)	55.0 (54.8)	4.2 (4.3)	2.2 (2.1)	4.7 (4.6)
ETOLH	Yellow orange	80	14.8 (14.7)	4.6 (4.7)	5.1 (5.2)	59.5 (59.4)	4.7 (4.8)	2.1 (2.0)	4.3 (4.5)
PPH	Red	88	14.1 (14.3)	4.4 (4.5)	5.1 (5.0)	59.5 (59.3)	4.5 (4.4)	6.0 (5.9)	4.6 (4.4)
TPH	Reddish violet	75	16.3 (16.4)	5.2 (5.2)	5.7 (5.8)	56.3 (56.5)	4.0 (3.9)	4.4 (4.5)	5.2 (5.0)

d, decomposes; melting points are uncorrected.

Table V.3. Comparison of major IR bands of ligands with those of respective complexes

Compound	ν(NH)	ν(CO)	ν(CS)	Thioamide bands				Mode of Coordination
				I	II	III	IV	
EPH	3330s 3240m	1735s	1120s	1530s,br	1290m	1020m	870m	
$[RuCl_2(AsPh_3)(EPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	3300w,br	1760s,br	1110m	1555s	1280m	1010w 1000w	870m	S
ETH	3240s,br	1730s	1180s	1510s,br	1360s	1020s	770s	
$[RuCl_2(AsPh_3)(ETH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	–	1760s	1170s	1525s	1370m	1050s	750s	S
ETOLH	3220s	1765s	1130m	1540s	1360s	1030s	850m	
$[RuCl_2(AsPh_3)(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	–	1170s	1100s	1580m	1345w	1010s	820m	S
PPH	3410m 3260m 3160m	1720s	1125s	1520s	1350s	1000m	860m	
$[RuCl_2(AsPh_3)(PPH)_2]_2$	3300br	1750s	1180m	1490m	1370s	1020w	865m	N
TPH	3200m	1760s	1140s	1555s	1305s	1000m	750s	
$[RuCl_2(AsPh_3)(TPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	–	1780m,br	1150s	1490m	1320s	1020w	750s	N

Table V.4. Major IR bands of the complexes and ligands

Compound	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands				Mode of Coordination
				I	II	III	IV	
EPH	3330s 3240m	1735s	1120s	1540s,br	1290m	1020m	870m	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(EPH)]$	3300br	1760s	1100s	1550m	1280m	1010m	850br	S
ETH	3240s,br	1730s	1180s	1510s,br	1360s	1020s	770s	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(ETH)]$	–	1750s	1180s	1480s	1360s	1000w	760s	N
ETOLH	3220s	1765s	1130m	1540s	1360s	1030m	850m	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(ETOLH)]$	–	1780m	1100s	1620m	1370w	1015m	850m	S
PPH	3410m 3260m 3160m	1720s	1125s	1520s	1350s	1000m	860m	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(PPH)]$	3400w	1750s	1180m	1480s	1360m	–	860m	N
TPH	3200m	1760m	1140s	1555s	1305s	1000m	750s	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(TPH)]$	–	1780s	1150s	1490s	1320s	1010m	750s	N

Table V.5. Electronic spectra of the ligands and complexes in chloroform and ^{1}H NMR spectra of the complexes in $CDCl_3$

Compound	Band position λ_{max} (nm)	Assignment	NMR signals with assignments (δ)
1	2	3	4
EPH	365	$\pi \longrightarrow \pi^*$	
	450	$n \longrightarrow \pi^*$	
ETH[a]	292	$\pi \longrightarrow \pi^*$	
	350	$n \longrightarrow \pi^*$	
ETOLH	275	CT	
	310	$\pi \longrightarrow \pi^*$	
	455	$n \longrightarrow \pi^*$	
PPH	390	$\pi \longrightarrow \pi^*$	
	415	$n \longrightarrow \pi^*$	
TPH	275	CT	
	285	CT	
	330	$\pi \longrightarrow \pi^*$	
	370	$n \longrightarrow \pi^*$	
$[RuCl_2(AsPh_3)(EPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	270sh	CT	
	355	IL	
	440w,sh	$^1A_{1g} \longrightarrow {}^1T_{2g}$	

Table V.5 (contd.)

1	2	3	4
$[RuCl_2(AsPh_3)(ETH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	335 525	IL $^1A_{1g} \rightarrow {}^1T_{1g}$	1.3 (br, 12 H, -CH$_3$), 4.2 (q, 8 H, -OCH$_2$), 5.3 (s, CH$_2$Cl$_2$) and 6.9-7.7 (m, 42 H, aromatic)
$[RuCl_2(AsPh_3)(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	270sh 315 480br	CT IL $^1A_{1g} \rightarrow {}^1T_{2g}$	1.2-1.4 (br, 12 H, -CH$_3$), 2.4 (s, 12 H, ring -CH$_3$), 4.2 (q, 8 H, -OCH$_2$), 5.4 (s, CH$_2$Cl$_2$), 7.2-7.8 (m, 46 H, aromatic) and 11.0 (s, 4 H, NH)
$[RuCl_2(AsPh_3)(PPH)_2]_2$	355 515br	IL $^1A_{1g} \rightarrow {}^1T_{1g}$	7.1-7.4 (m, aromatic)
$[RuCl_2(AsPh_3)(TPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$	280 375 555	CT IL $^1A_{1g} \rightarrow {}^1T_{1g}$	5.3 (s, CH$_2$Cl$_2$), 6.4 (m, 4 H, pyrrolyl CH), 6.8 (m, 4 H, pyrrolyl CH) and 7.3-7.7 (m, 34 H, aromatic and pyrrolyl CH)

a, in ethanol; w, weak; br, broad; sh, shoulder.

Table V.6. Electronic spectra of the complexes in chloroform and proton NMR in CDCl$_3$

1	2	3	4
Compound	Band position* λ_{max} (nm)	Assignment	NMR signals with assignments (δ)
$[(\eta^5-C_5H_5)RuCl(PPh_3)(EPH)]$	475	$^1A_{1g} \longrightarrow {}^1T_{2g}$	1.3 (t, 3 H, -CH$_3$), 4.1 (s, 5 H, η^5-C$_5$H$_5$), 4.3 (q, 2 H, -OCH$_2$), 7.2-7.4 (m, 18 H, aromatic)
	355(-10)	IL ($\pi \longrightarrow \pi^*$)	
	270	CT	
	240	CT	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(ETH)]$	525sh	$^1A_{1g} \longrightarrow {}^1T_{1g}$	1.3 (t, 3 H, -CH$_3$), 4.1 (s, 5 H, η^5-C$_5$H$_5$), 4.3 (m, 2 H, -OCH$_2$), 7.0-7.7 (m, 18 H, aromatic)
	465	$^1A_{1g} \longrightarrow {}^1T_{2g}$	
	335(-15)	IL (n $\longrightarrow \pi^*$)	
	245	CT	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(ETOLH)]$	375br	IL or CT	1.2 (t, 3 H, -CH$_3$), 2.2 (br, 3 H, ring -CH$_3$), 4.2 (s, 5 H, η^5-C$_5$H$_5$), 4.4 (br, 2 H, -OCH$_2$), 7.1-7.4 (m, 19 H, aromatic)
	325sh(+15)	IL ($\pi \longrightarrow \pi^*$)	
	245	CT	
$[(\eta^5-C_5H_5)RuCl(PPh_3)(PPH)]$	485	$^1A_{1g} \longrightarrow {}^1T_{2g}$	4.1 (s, 5 H, η^5-C$_5$H$_5$), 7.0-7.6 (m, 23 H, aromatic)
	355	IL or CT	
	240	CT	

...contd.

Table V.6 (contd.)

1	2	3	4
$[(\eta^5-C_5H_5)RuCl(PPh_3)(TPH)$	468	$^1A_{1g} \longrightarrow {}^1T_{2g}$	4.1 (s, 5 H, $\eta^5-C_5H_5$),
	360(-10)	IL (n → π*)	7.0-7.5 (m, 18 H, aromatic)
	325sh(+5)	IL (π → π*)	
	310	CT	
	280sh(-5)	CT	
	270(-5)	CT	
	240	CT	

*br, broad; sh, shoulder.

The values given in parentheses ( ) indicate the shift in the position of respective ligands's band[9-11,14,15] after complexation.

LEGEND TO FIGURES

Fig. V.1   Infrared Spectra

1. $[RuCl_3(AsPh_3)_2(CH_3OH)]$
2. $[RuCl_2(AsPh_3)(PPH)_2]_2$
3. $[RuCl_2(AsPh_3)(EPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
4. $[RuCl_2(AsPh_3)(TPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
5. $[RuCl_2(AsPh_3)(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
6. $[RuCl_2(AsPh_3)(ETH)_2]_2 \cdot \frac{1}{2}CH_2CH_2Cl_2$
7. $[(\eta^5-C_5H_5)RuCl(PPh_3)_2]$
8. $[(\eta^5-C_5H_5)RuCl(PPh_3)(TPH)]$
9. $[(\eta^5-C_5H_5)RuCl(PPh_3)(ETH)]$
10. $[(\eta^5-C_5H_5)RuCl(PPh_3)(PPH)]$
11. $[(\eta^5-C_5H_5)RuCl(PPh_3)(ETOLH)]$
12. $[(\eta^5-C_5H_5)RuCl(PPh_3)(EPH)]$

Fig. V.2.1   Electronic Spectra

1. $[RuCl_2(AsPh_3)_2(TPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
2. $[RuCl_2(AsPh_3)_2(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
3. $[RuCl_2(AsPh_3)_2(EPH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
4. $[RuCl_2(AsPh_3)_2(ETH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
5. $[RuCl_2(AsPh_3)_2(PPH)_2]_2$

Fig. V.2.2   Electronic Spectra

1. $[(\eta^5-C_5H_5)RuCl(PPh_3)(ETOLH)]$
2. $[(\eta^5-C_5H_5)RuCl(PPh_3)(TPH)]$
3. $[(\eta^5-C_5H_5)RuCl(PPh_3)(PPH)]$
4. $[(\eta^5-C_5H_5)RuCl(PPh_3)(EPH)]$
5. $[(\eta^5-C_5H_5)RuCl(PPh_3)(ETH)]$

Fig. V.3 Proton NMR Spectra

1. $[RuCl_2(AsPh_3)(ETH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
2. $[RuCl_2(AsPh_3)(ETOLH)_2]_2 \cdot \frac{1}{2}CH_2Cl_2$
3. $[(\eta^5-C_5H_5)RuCl(PPh_3)(EPH)]$
4. $[(\eta^5-C_5H_5)RuCl(PPh_3)(ETH)]$
5. $[(\eta^5-C_5H_5)RuCl(PPh_3)(ETOLH)]$
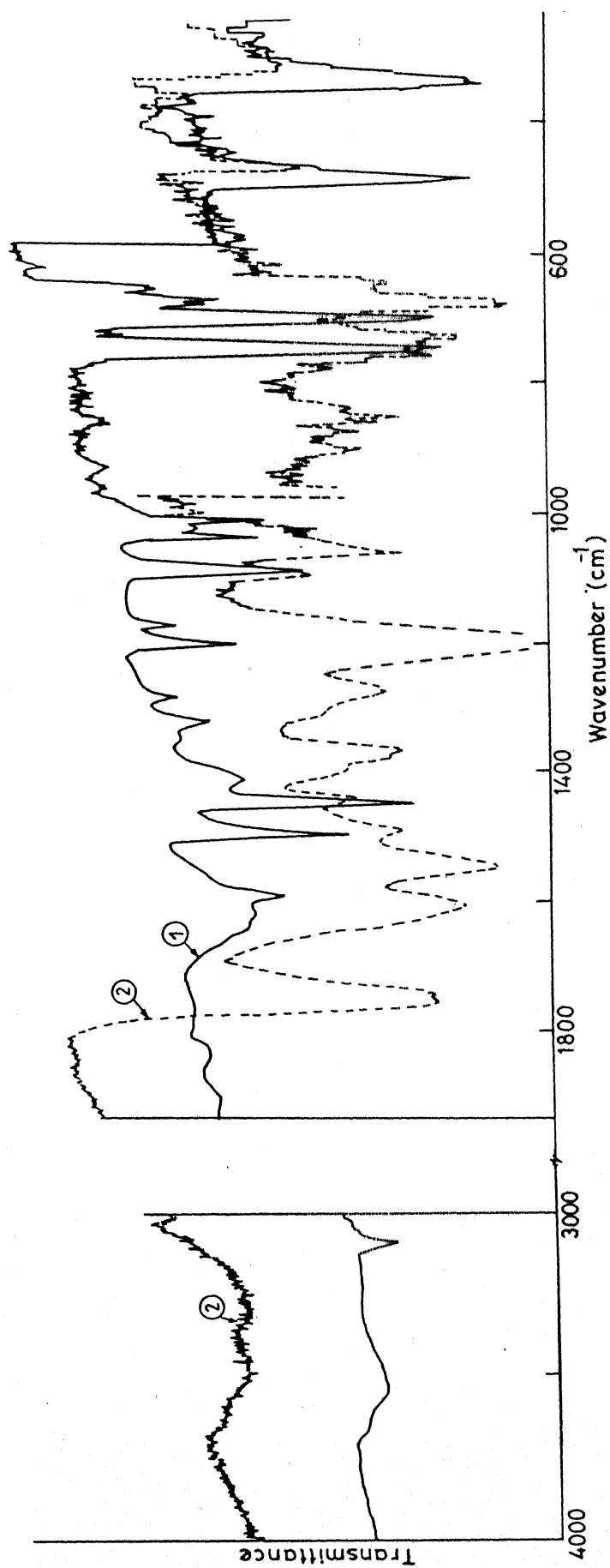
Fig.V.1 IR Spectra
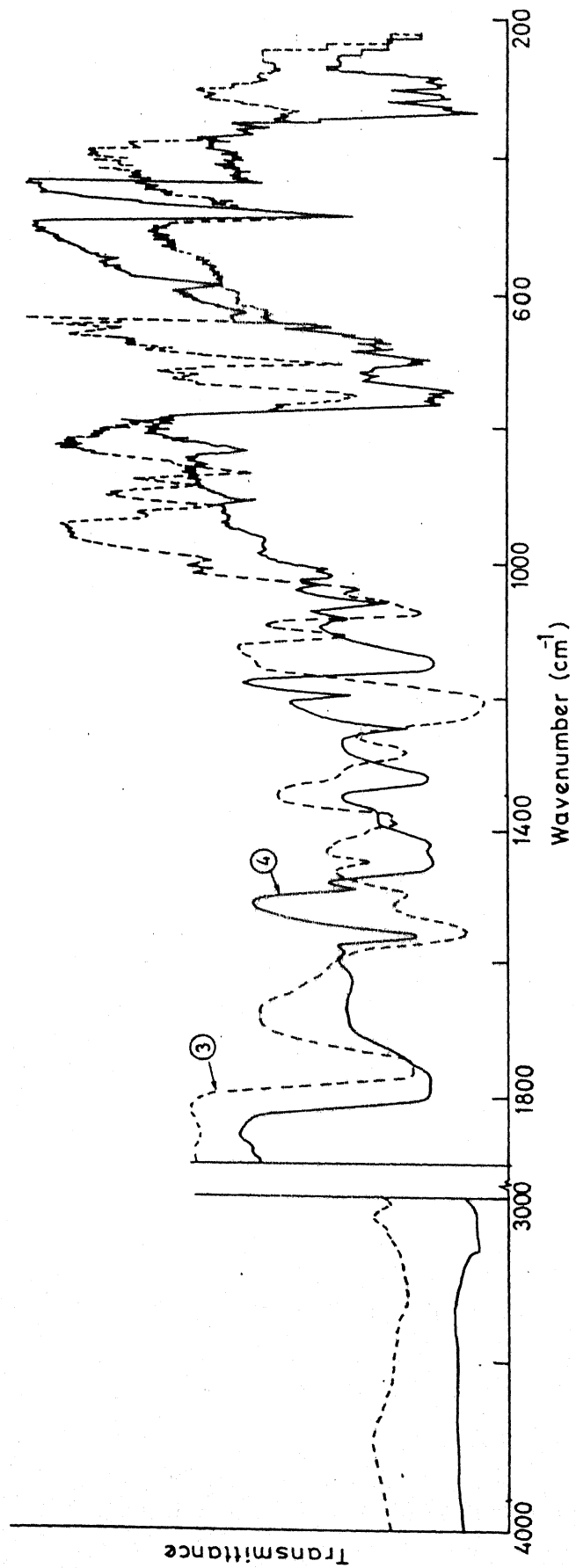
Fig. V.1   IR Spectra
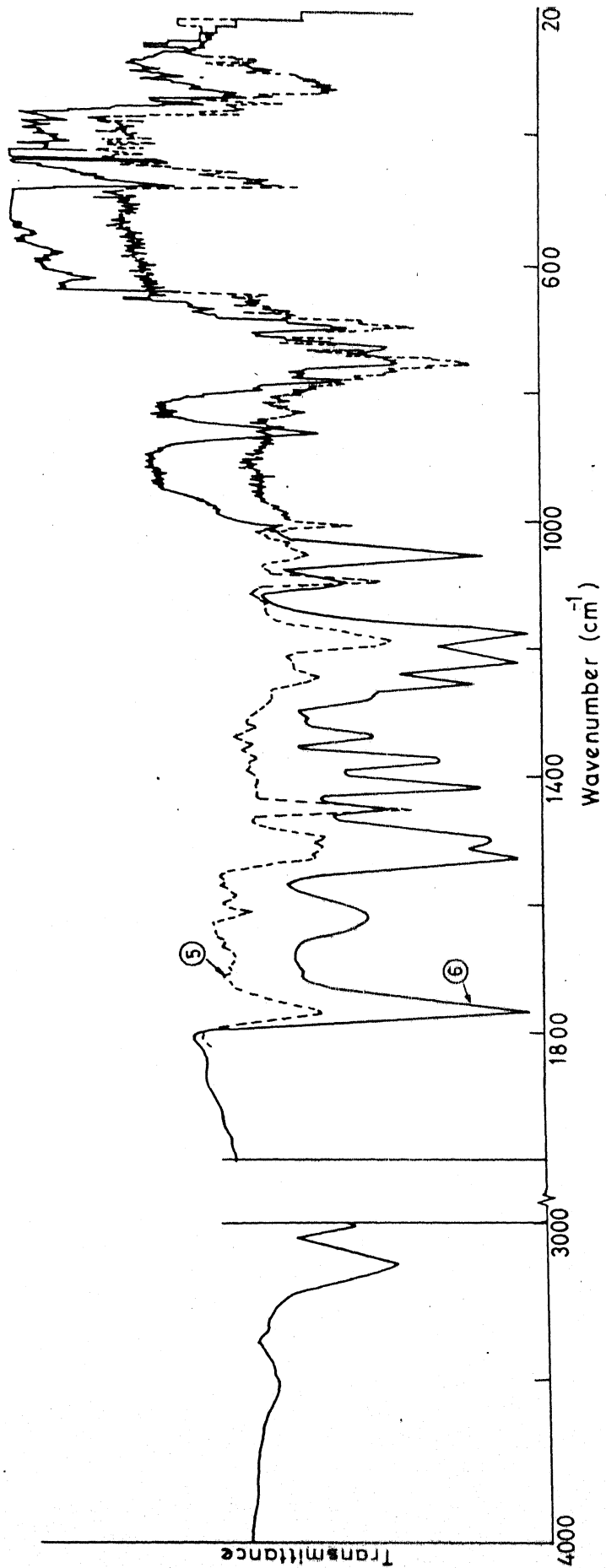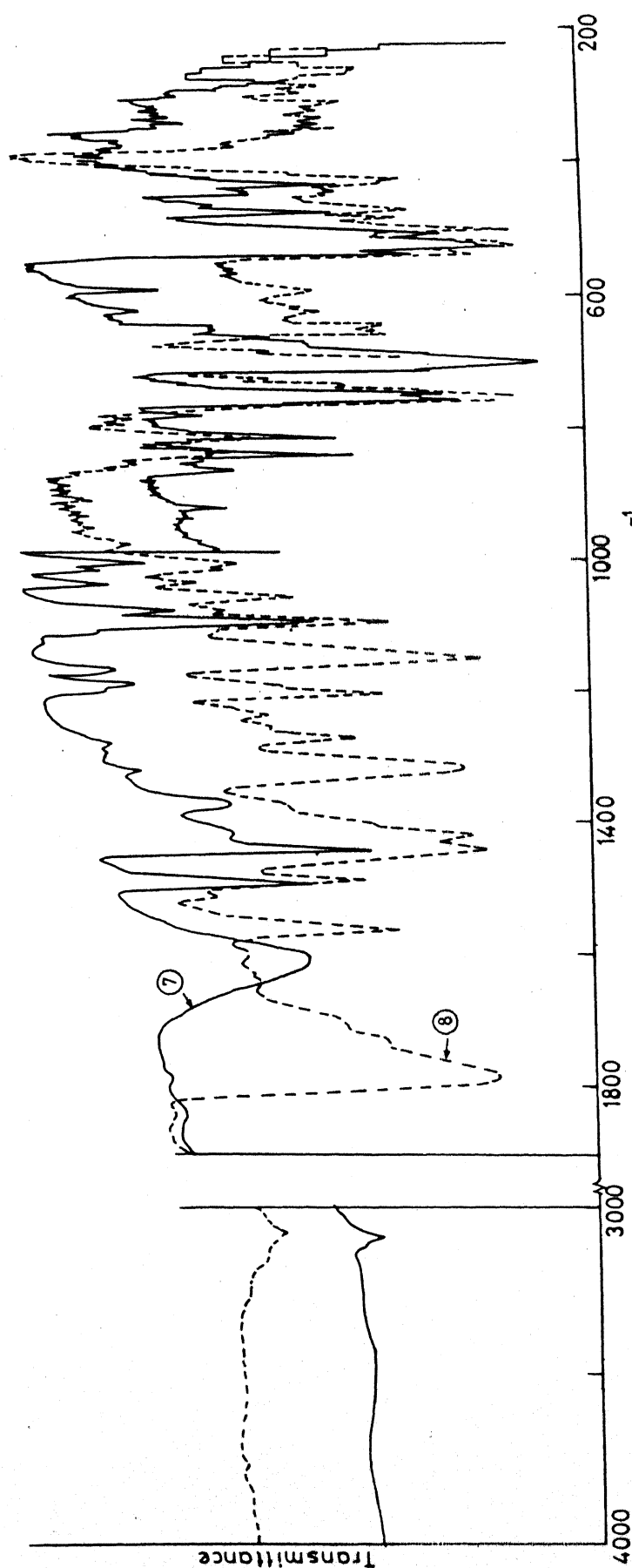
Fig. V.1 IR Spectra
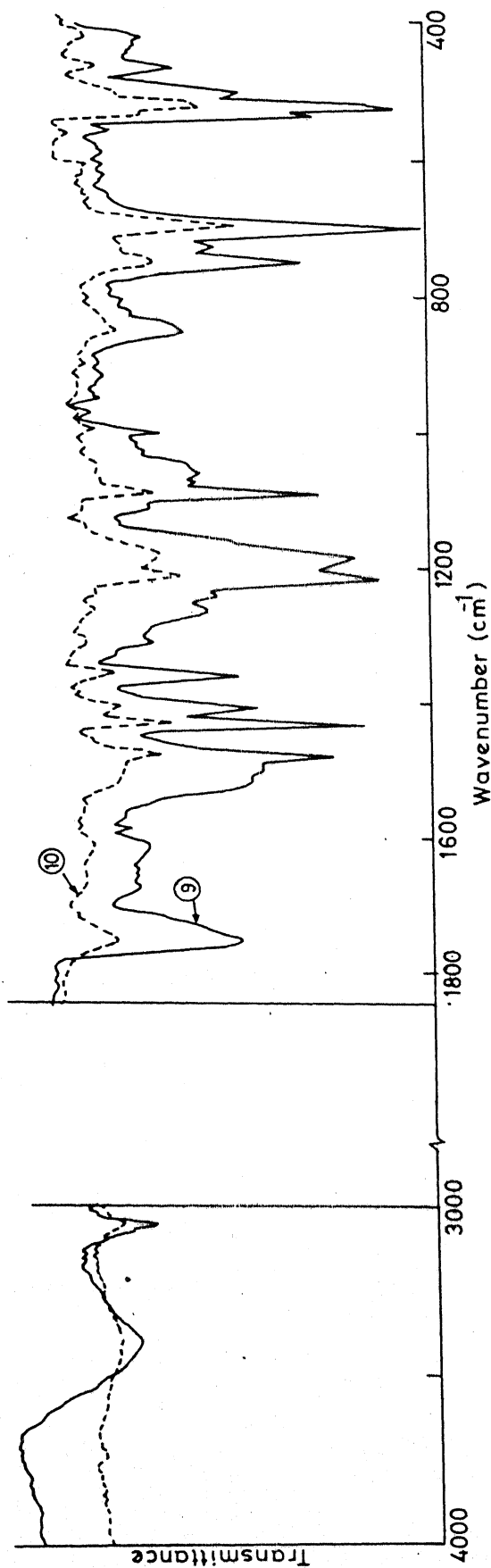
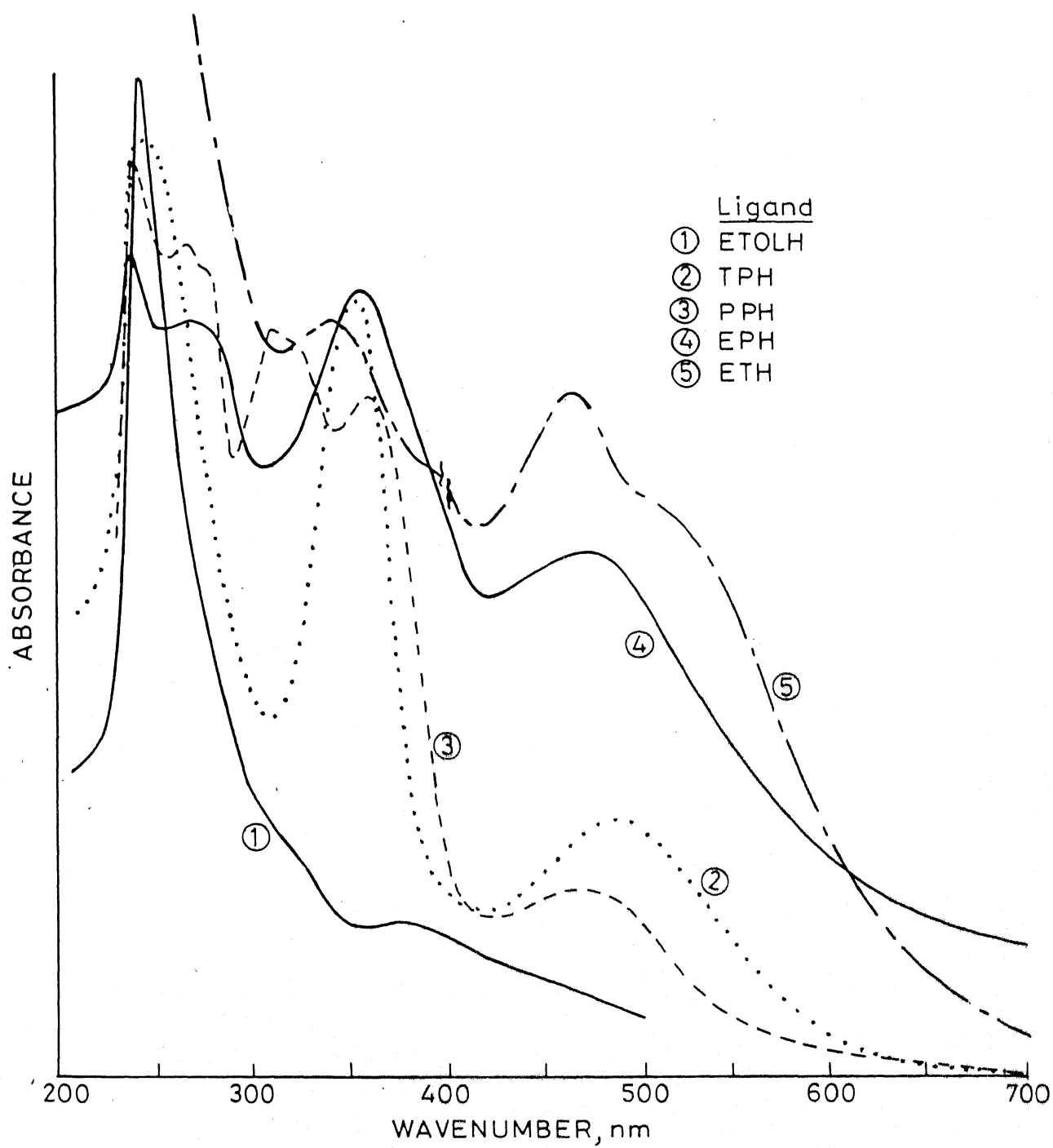Fig.V.1   IR Spectra
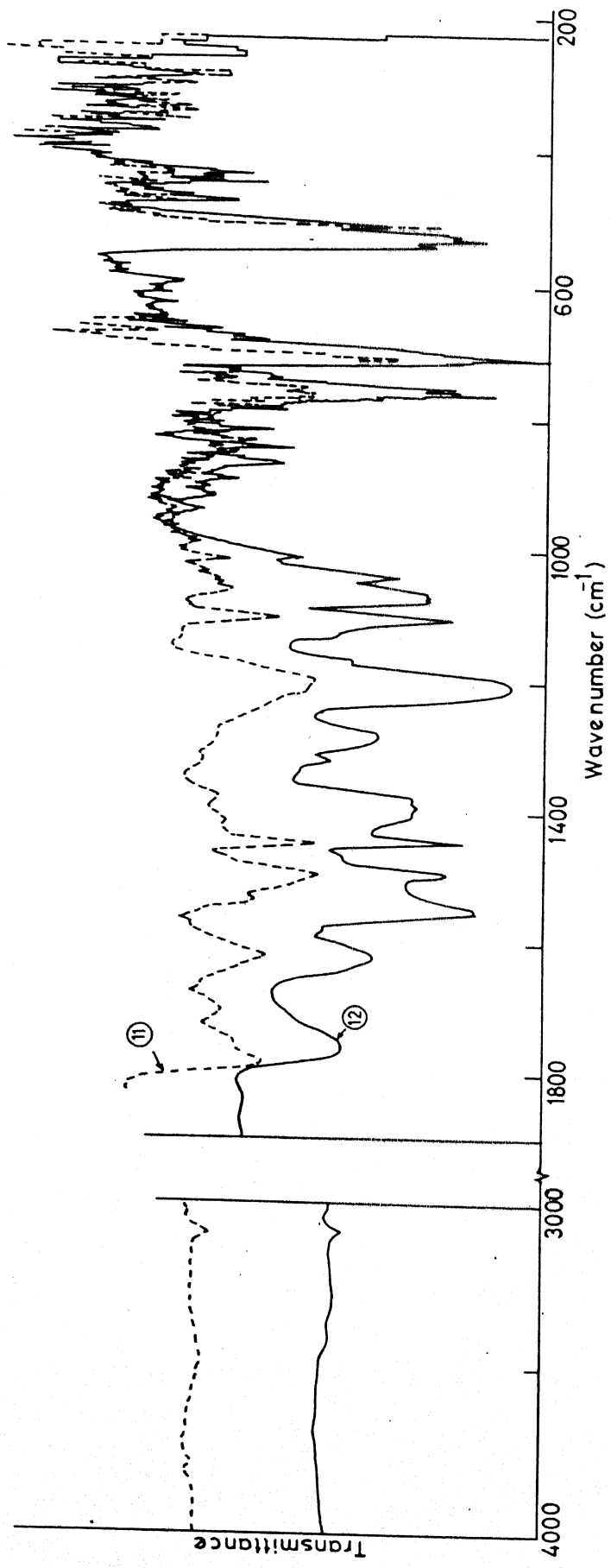
Fig.V.1   IR Spectra

Fig. V.1   IR Spectra

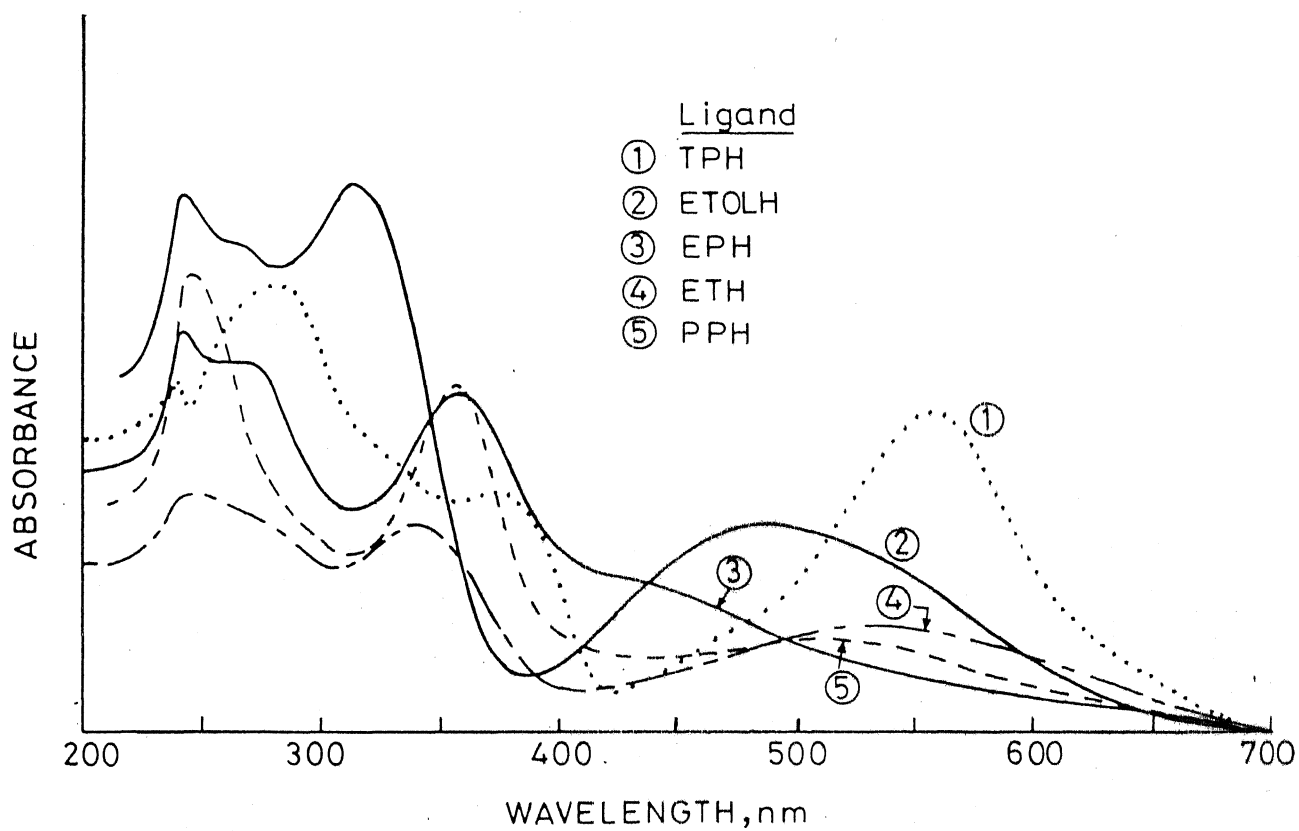Fig.V.2.1 Electronic spectra of $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)(ligand)]$

Ligand
① ETOLH
② TPH
③ PPH
④ EPH
⑤ ETH

Fig. V. 2.2 Electronic spectra of $[RuCl_2(AsPh_3)(ligand)_2]_2 \frac{1}{2} CH_2Cl_2$
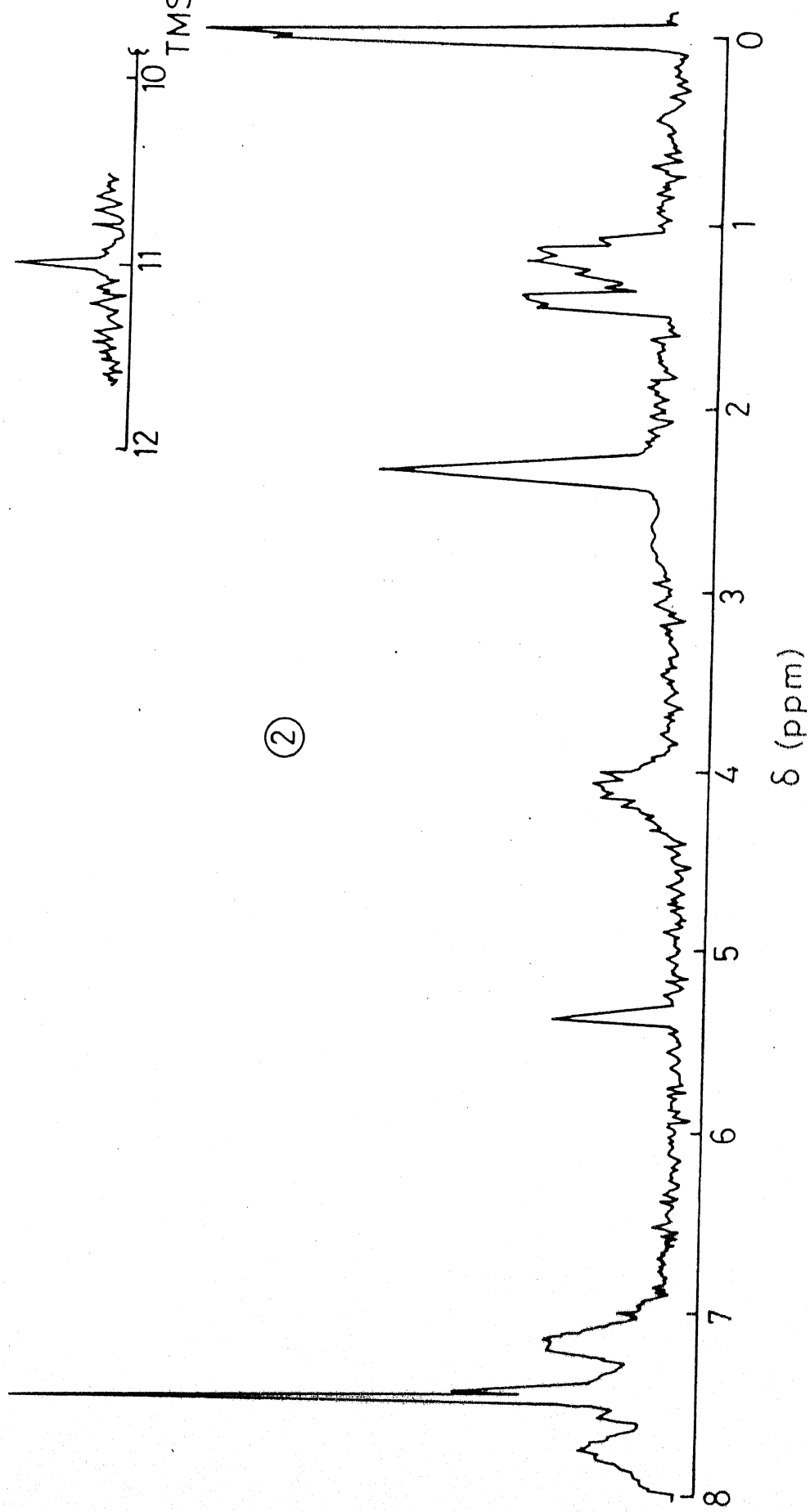
TMS
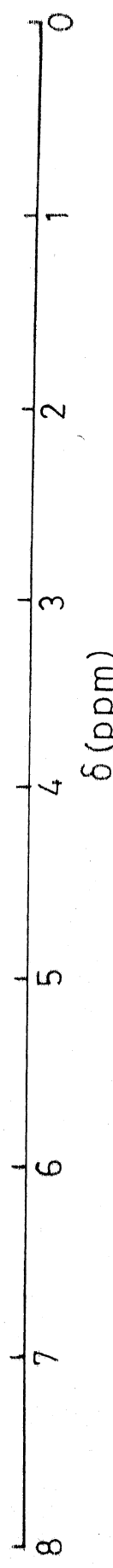
δ(ppm)

①

Fig. V.3 Proton NMR spectra
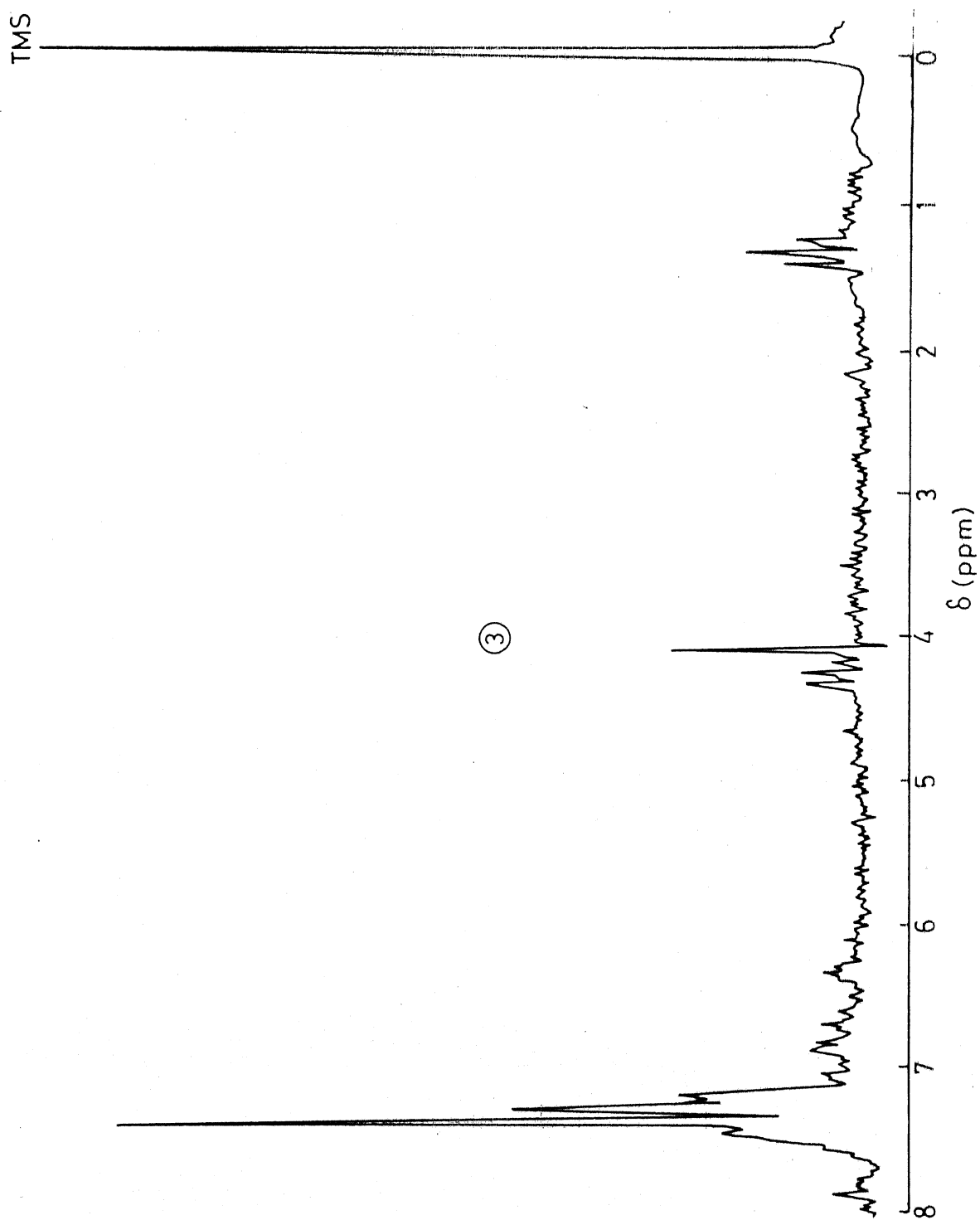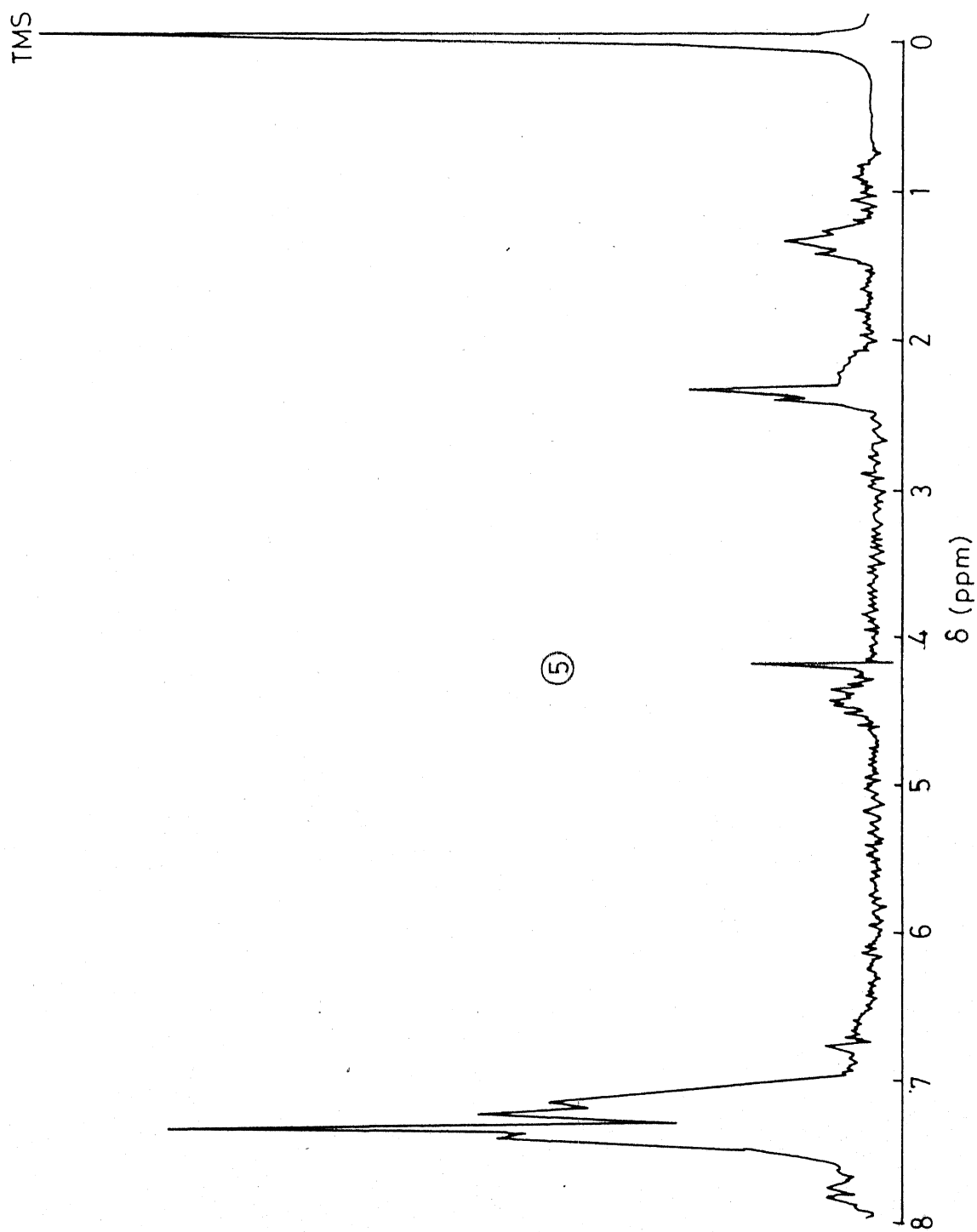
Fig.V.3 Proton NMR spectra
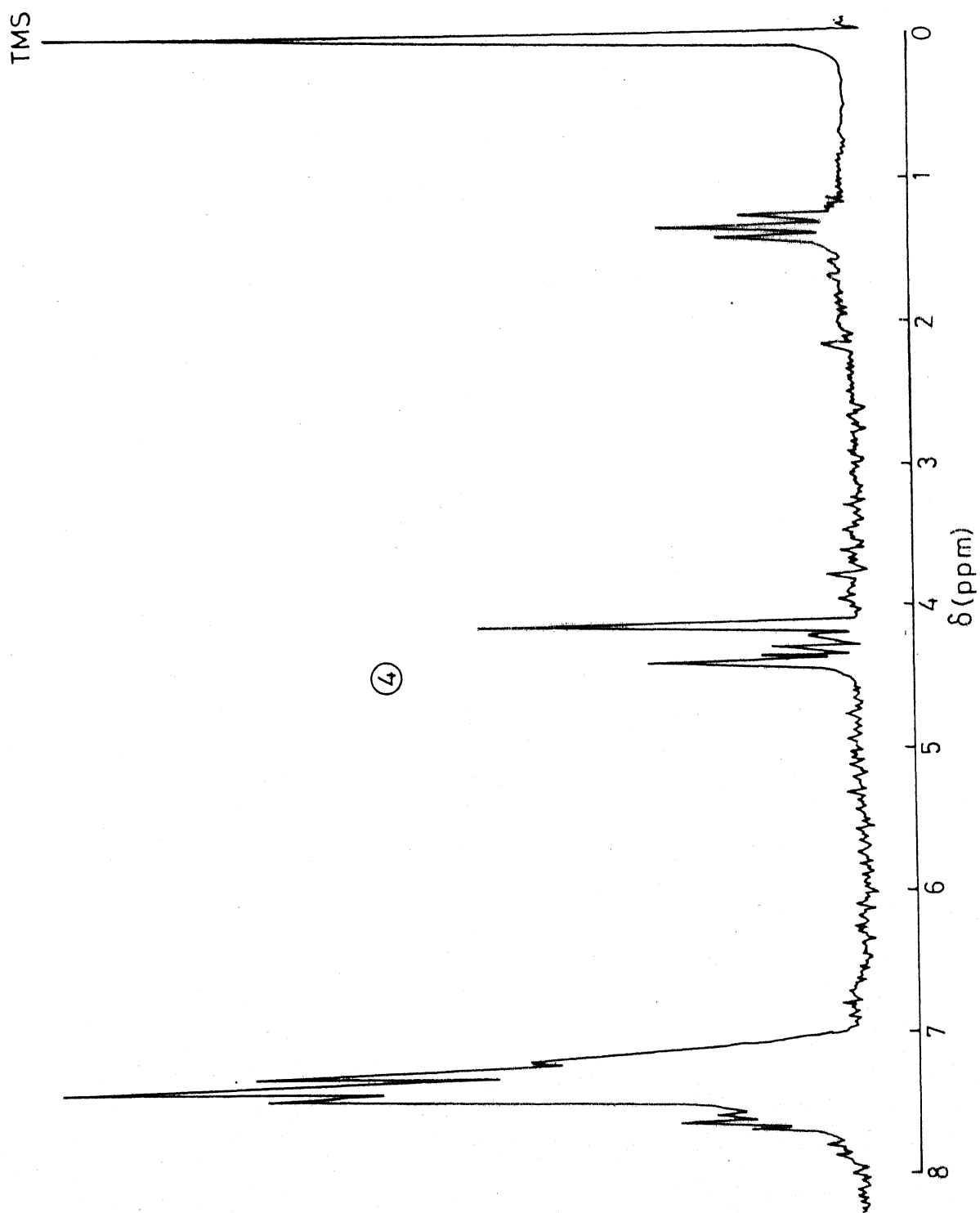
Fig. V.3 Proton NMR spectra

Fig.V.3 Proton NMR spectra

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Chapter VI

MIXED RHODIUM(I) CARBONYLS: REACTIONS OF
trans-$[Rh(CO)Cl(MPh_3)_2]$ (M = P or As)
WITH SOME THIOCARBOXA(I)MIDES

In this chapter, the reactions of trans-$[Rh(CO)Cl(MPh_3)_2]$
(M = P or As) with some thiocarboxamides of type $R_1-C(S)NHC(O)-R_2$
(R_1, R_2 are substituents of wide variety) and 2-thiopyrrole-1,2-
dicarboximide have been described. These reactions in chloroform
led to the formation of mixed ligand Rh(I) complexes of the type
$[Rh(CO)Cl(MPh_3)(ligand)]\cdot\frac{1}{3}CHCl_3$. These complexes were characte-
rised by means of analytical, magnetic and spectral (i.r., u.v.,
visible and ^{1}H NMR) studies. The ligands are coordinated as
neutral unidentate ligand. The square planar geometry for the
complexes has been proposed.

VI.1 EXPERIMENTAL

All the chemicals used were either of AnalaR or chemically
pure grade. Dried solvents were used. The details of methods of
analyses, magnetic and spectral studies have been described in

previous chapters (II-V).

The estimation of rhodium was made on a IL-751 atomic absorption spectrophotometer. The sensitivity of this instrument for rhodium is 0.2 μg/ml to 20 μg/ml (rhodium concentration of solution). Five standard solutions of rhodium concentrations 1 μg/ml, 5 μg/ml, 10 μg/ml, 15 μg/ml and 20 μg/ml were prepared for the estimation.

VI.1.1a Preparation of Standard Solutions for Rhodium Analyses

0.00965 g of ammonium hexachlororhodate $\left[(NH_4)_3RhCl_6\right]$ was dissolved in 10 ml of 1:10 HCl and diluted to a volume of 50 ml with 1:10 HCl. The concentration of resulting solution is 50 μg/ml of rhodium. From this stock solution, five solutions were prepared, viz., 1 μg/ml, 5 μg/ml, 10 μg/ml, 15 μg/ml and 20 μg/ml by diluting with distilled water

b. Preparation of Sample Solutions of Rhodium Complexes

A weighed amount, about 4-6 mg of the complex (this solution should have the concentration in the range of five standard solutions) was decomposed by heating with mixture of HNO_3 and H_2SO_4 upto almost dryness several times until the resulting residue gave clear solution in water. It was filtered and filtrate was diluted with distilled water to a volume of 100 ml.

The preparations of ligands EPH, ETH, PPH and TPH are described in Chapter V. The ligand N-ethoxycarbonylpyrrole-1-

thiocarboxamide (EPTH) and the parent compounds trans-[Rh(CO)Cl-(MPh$_3$)$_2$] (M = P or As) were prepared by following literature methods.

VI.1.2   Preparation of N-Ethoxycarbonylpyrrole-1-thiocarboxamide (EPTH)[1]

Pyrrole-potassium was prepared in nitrogen atmosphere by the gentle refluxing of a stirred mixture of 40.2 g (0.60 mol) of pyrrole, 100 ml of THF and 19.5 g (0.50 g.atom) of potassium, until all the metal had reacted. Following dilution with 150 ml of solvent and chilling of the slurry in an ice-salt bath, there was introduced a solution of 59.0 g (0.45 mol) of ethoxycarbonyl-isothiocyanate in 100 ml of THF, dropwise, at such a rate, the reaction temperature was kept below 10°C (addition time 1.5 hr). The reaction mixture was stirred for a further 0.5 hr, then it was mixed with 1 lit. of absolute ether and filtered. The pota-ssium salt, thus obtained was dissolved in water, and the result-ing solution was washed with ether, chilled and acidified with acetic acid. Filtration (yield, 39.8 g; 45%) of crude, m.p. 77-80°C and recrystallisation from petroleum ether (60-80°C) afford-ed the pure compound as yellow needles, m.p. 80-81°C.

VI.1.3   Preparation of trans-[Rh(CO)Cl(MPh$_3$)$_2$],[2] (M = P or As)

RhCl$_3$.3H$_2$O (2.0 g, 0.0076 mol) in 70 ml of absolute etha-nol is slowly added to 300 ml of boiling ethanol containing about a two-fold excess* of PPh$_3$ (7.2 g, 0.0275 mol). The

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*If a stoichiometric quantity is used, the product is contaminated and is in low yield.

solution which may be turbid, becomes clear in about 2 min. Then sufficient (10-20 ml) 37% formaldehyde solution is added to cause the red solution to become pale yellow in about one minute, and yellow micro-crystals to precipitate. After cooling, the collected crystals are washed with ethanol and diethyl ether and dried in air or vacuum. They can be recrystallised from minimum quantity of hot benzene (yield, 4.5 g; 85% based on $RhCl_3 \cdot 3H_2O$). The triphenylarsine complex was prepared in an analogous manner, m.p. 195-197°C (phosphine complex) and 242-244°C (arsine complex).

VI.1.4 General Method for Preparation of the Complexes $\left[Rh(CO)Cl(MPh_3)(LH) \right] \cdot \frac{1}{3} CHCl_3$, (M = P or As); (LH = EPH, ETH, PPH, TPH or EPTH)
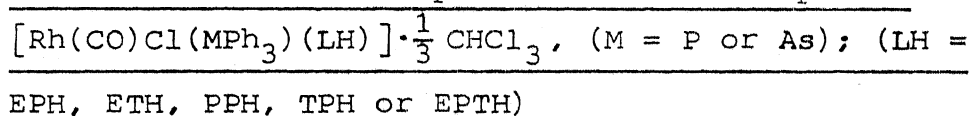
To 25 ml of chloroform solution containing 0.5 mmol $\left[Rh(CO)Cl(MPh_3)_2 \right]$, 25 ml of chloroform solution containing 0.75 mmol of appropriate ligand was added slowly under dry N_2. The mixture was refluxed for an hour on water bath, resulting solution was filtered off (if needed) and concentrated to 5 ml at reduced pressure, followed by an addition of excess ($\sim$50 ml) petroleum ether (40-60°), immediate yellow to reddish brown precipitates appeared which were centrifuged and washed with petroleum ether and dried in vacuo.

VI.2 RESULTS AND DISCUSSION

All compounds are diamagnetic, non-ionic, generally air stable and soluble in most of the organic solvents. Analytical

results are consistent with stoichiometry proposed (Table VI.1).

VI.2.1 IR Spectra

The coordination site of the ligands as given in Table VI.2 is the result of careful comparison of important IR bands of the ligand with the respective complex. The thioamide band I (δ_{N-H} + ν_{C-N}) reasonably shifted to lower or higher frequency in most of the complexes. Red shift of thioamide band I indicates, coordination through N whereas blue shift for the band implies coordination through sulphur. In case of coordination through sulphur, the $\nu(C=S)$ and thioamide band IV ($\nu_{C=S}$) either shift to lower wave number or remain unchanged with reduced intensity. Blue shift in band IV and $\nu(C=S)$ was taken as a proof for non-involvement of thiocarbonyl group in coordination. The thioamide band II (ν_{C-N} + $\nu_{C=S}$ + δ_{C-H}) and band III (ν_{C-N} + ν_{C-S}) did not shift systematically hence could not be used reliably for deciding bonding site. The coordination through ring nitrogen or sulphur of pyrrole or thiophene is unlikely as they are weakly basic. The $\nu(NH)$ in some of the complexes becomes too weak and broad to be detected. The $\nu(C=O)$ of the ligands shift invariably to higher frequency after complexation, hence coordination through oxygen is ruled out. The terminal $\nu(C\equiv O)$ shifts to higher frequencies ($+25$ to 160 cm^{-1}). The increase in the stretching frequency of carbon monoxide may be because of higher π-acidity of the thio-carboxa(i)mides as compared to PPh$_3$/AsPh$_3$. Large blue shift in $\nu(C\equiv O)$ may be because of the presence of PPh$_3$ or AsPh$_3$ or thio-

carboxa(i)mides trans- to CO instead of chloride ion, unusually high values of $\nu(C\equiv O)$ terminal in most of these complexes are quit surprising. All characteristic bands of $PPh_3/AsPh_3$[3,4] were present in the all i.r. spectra of the complexes. The new bands of weak to medium intensity at 300-500 cm^{-1} may be assigned to coupled vibrations of $\nu(Rh-Cl)$, $\nu(Rh-N)$ or $\nu(Rh-S)$.[5]

VI.2.2 Electronic Spectra

In the electronic spectra (Table VI.3 of complexes, no d-d transitions were observed probably because they were masked by strong change transfer (CT) and/or intraligand (IL) bands or continuous absorption in the visible region. However, a weak shoulder at 510 nm was observed in the electronic spectrum of $[Rh(CO)Cl(PPh_3)(EPH)]\cdot\frac{1}{3}CHCl_3$. In square-planar Rh(I) complexes (d^8-system), three spin allowed d-d transitions, $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1B_{1g}$ and ^1E_g, are anticipated. Besides these, three spin forbidden $^1A_{1g} \rightarrow {}^3A_{2g}$, $^3B_{1g}$ and ^3E_g transitions are also expected but these are too weak to be observed. The transition $^1A_{1g} \rightarrow {}^1E_g$ is relatively intense and occur at high energy, ca. 440 nm. Therefore, the observed transition at 510 nm may be assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ or $^1B_{1g}$. The intense and high energy bands present in the complexes may be due to charge transfer or intraligand transitions.

VI.2.3 NMR Spectra

The proton NMR spectra of some of the complexes were taken in $CDCl_3$ (Table VI.3). All the characteristic signals of ligands and PPh_3/$AsPh_3$ were present in the spectra of the complexes. However, NH proton resonance could not be observed. The chloroform resonance (δ, 7.27) was probably merged with aromatic protons.

Table VI.1. Analytical data of the complexes

Compound	Colour	M.p.*[^] (°C)	Analyses: Found (Calcd.), %						
			Rh	S	Cl	C	H	N	P/A
[Rh(CO)Cl(PPh₃(EPH)]·⅓CHCl₃	Greenish yellow	140	15.2 (15.4)	4.9 (4.8)	10.7 (10.6)	49.0 (49.2)	3.7 (3.8)	4.4 (4.2)	4.4 (4.6)
[Rh(CO)Cl(AsPh₃)(EPH)]·⅓CHCl₃	Yellow	143	14.6 (14.5)	4.6 (4.5)	10.2 (10.0)	46.3 (46.2)	3.5 (3.6)	4.0 (3.9)	– (10.͘)
[Rh(CO)Cl(AsPh₃)(ETH)]·⅓CHCl₃	Reddish brown	97	14.0 (14.2)	8.9 (8.8)	10.0 (9.8)	45.0 (45.1)	3.3 (3.3)	1.7 (1.9)	– (10.͘)
[Rh(CO)Cl(PPh₃)(PPH)]·⅓CHCl₃	Dirty yellow	165	14.5 (14.4)	4.4 (4.5)	10.2 (10.0)	52.8 (52.7)	3.8 (3.7)	6.0 (5.9)	4.2 (4.͘)
[Rh(CO)Cl(AsPh₃)(PPH)]·⅓CHCl₃	Yellow	115	13.4 (13.6)	4.4 (4.2)	9.5 (9.4)	50.2 (50.0)	3.4 (3.4)	5.7 (5.5)	(9.9)
[Rh(CO)Cl(PPh₃)(EPTH)]·⅓CHCl₃	Yellowish brown	195	15.8 (15.5)	4.9 (4.8)	10.6 (10.7)	49.5 (49.3)	3.8 (3.7)	4.1 (4.2)	4.6 (4.7)
[Rh(CO)Cl(AsPh₃)(EPTH)]·⅓CHCl₃	Reddish brown	101	14.4 (14.5)	4.6 (4.5)	9.9 (10.0)	46.1 (46.2)	3.5 (3.4)	4.0 (3.9)	– (10.6)
[Rh(CO)Cl(PPh₃)(TPH)]·⅓CHCl₃	Dirty yellow	155d	16.6 (16.6)	5.3 (5.2)	11.5 (11.4)	49.2 (49.0)	3.0 (3.1)	4.3 (4.5)	5.2 (5.0)
[Rh(CO)Cl(AsPh₃)(TPH)]·⅓CHCl₃	Yellowish brown	94	15.4 (15.5)	4.9 (4.8)	10.9 (10.7)	45.7 (45.8)	2.7 (2.9)	4.1 (4.2)	– (11.3)

*Melting points are uncorrected.

Table VI.2. Comparison of major IR bands of the ligands and complexes

Compound	ν(NH)	ν(C≡O) terminal	ν(C=O) ligand	(C=S)	I	II	III	IV	Mode of Coordination
1	2	3	4	5	6	7	8	9	10
EPH	3300s 3240m	–	1735s	1120s	1540s	1290m	1020m	870m	
[Rh(CO)Cl(PPh$_3$)(EPH)]·$\frac{1}{3}$CHCl$_3$	3250br	2110s	1750s	1100s	1550s	1280s	1030w	860m	S
[Rh(CO)Cl(AsPh$_3$)(EPH)]·$\frac{1}{3}$CHCl$_3$	3200w,br	2125s	1760s	1100w 1070m	1550m	1280w	1035m	870m	S
ETH	3240s	–	1730s	1180s	1510s,br	1360s	1020s	770s	
[Rh(CO)Cl(AsPh$_3$)(ETH)]·$\frac{1}{3}$CHCl$_3$	–	2140s	1770s	–	1530m	1370w	1010m	750s	S
PPH	3410m 3280m 3160m	–	1720s	1125s	1520s	1350s	1000m	860m	
[Rh(CO)Cl(PPh$_3$)(PPH)]·$\frac{1}{3}$CHCl$_3$	3410m 3260w 3160w	1995s	1710s	1120s 1110s	1570s,br 1550	1340s	1010m	860m	S
[Rh(CO)Cl(AsPh$_3$)(PPH)]·$\frac{1}{3}$CHCl$_3$	3320s 3080s	2130s	1710m	1140m	1510s 1490s	1340s	1010m	850w 900m	N
EPTH	3250m	–	1750s	1130m	1540m,br	1360m	1025m	780m	

...contd.

Table VI.2. (contd.)

1	2	3	4	5	6	7	8	9	10
$[Rh(CO)Cl(PPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$	-	2130s	1800m	1100s	1610m,br	1340w	1010m	750s	S
$[Rh(CO)Cl(AsPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$	-	2130m	1800m	1100s,t	1540m	1345m	1010m	750s	S
TPH	3200m	-	1763s 1750s	1140s	1555s	1305s	1000m	750s	
$[Rh(CO)Cl(PPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$	-	2140s,br	1760m 1800m	1150m	1500m	1340w	1010w	760s	N
$[Rh(CO)Cl(AsPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$	3180w,br	2140s	1760m 1800m	1140s	1500m	1340s	1010m	760s	N

w, weak; m, medium; s, strong; t, triplet; br, broad.

Table VI.3. The electronic spectra of the complexes in chloroform and proton NMR spectra in CDCl$_3$

Compound	Band position λ_{max} (nm)	Assignment	^{1}H NMR signals and their assignments (δ)
1	2	3	4
[Rh(CO)Cl(PPh$_3$)(EPH)]·$\frac{1}{3}$CHCl$_3$	510w,sh	$^1A_{1g} \rightarrow {^1A_{2g}}$ or $^1B_{1g}$	1.3 (t, 3 H, -CH$_3$),
	420(-30)	IL	4.3 (q, 2 H, -OCH$_2$),
	265w,sh	CT	6.7-7.8 (m, 18 H, aromatic)
[Rh(CO)Cl(AsPh$_3$)(EPH)]·$\frac{1}{3}$CHCl$_3$	380sh(+15)	IL ($\pi \rightarrow \pi^*$)	1.3 (t, 3 H, -CH$_3$),
	315	CT	4.3 (q, 2 H, -OCH$_2$),
	260	CT	6.7-7.8 (m, 18 H, aromatic)
[Rh(CO)Cl(AsPh$_3$)(ETH)]·$\frac{1}{3}$CHCl$_3$	330(-20)	IL ($n \rightarrow \pi^*$)	1.3 (t, 3 H, -CH$_3$),
	270(-22)	IL ($\pi \rightarrow \pi^*$)	4.3 (q, 2 H, -OCH$_2$),
			7.3-7.8 (m, 18 H, aromatic)
[Rh(CO)Cl(AsPh$_3$)(PPH)]·$\frac{1}{3}$CHCl$_3$	315	CT	6.6-7.2 (m, aromatic protons)
	285	CT	
	250	CT	

Table VI.3 (contd.)

1	2	3	4
$[Rh(CO)Cl(PPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$	300sh	CT	
	275w	CT	
$[Rh(CO)Cl(AsPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$	260	CT	
$[Rh(CO)Cl(PPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$	375w,sh(+5)	IL (n $\rightarrow$ π*)	
	310sh(-20)	IL (π $\rightarrow$ π*)	
	265	CT	
$[Rh(CO)Cl(AsPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$	390w,sh(+20)	IL (n $\rightarrow$ π*)	7.4-7.8 (m, aromatic)
	300(-30)	IL (π $\rightarrow$ π*)	
	260	CT	

w, weak; sh, shoulder.

The values given in the parentheses ( ) indicate the shift in the position of respective ligand's band[7-11] after complexation.

LEGEND TO FIGURES

Fig. VI.1   Infrared Spectra

1. trans-$[RhCO)Cl(AsPh_3)_2]$
2. $[Rh(CO)Cl(AsPh_3)(ETH)]\cdot\frac{1}{3}CHCl_3$
3. $[Rh(CO)Cl(AsPh_3)(EPH)]\cdot\frac{1}{3}CHCl_3$
4. $[Rh(CO)Cl(PPh_3)(EPH)]\cdot\frac{1}{3}CHCl_3$
5. $[Rh(CO)Cl(AsPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$
6. $[Rh(CO)Cl(PPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$
7. $[Rh(CO)Cl(AsPh_3)(PPH)]\cdot\frac{1}{3}CHCl_3$
8. $[Rh(CO)Cl(PPh_3)(PPH)]\cdot\frac{1}{3}CHCl_3$
9. $[Rh(CO)Cl(AsPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$
10. $[Rh(CO)Cl(PPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$

Fig. VI.2.1   Electronic Spectra (in $CHCl_3$)

1. $[Rh(CO)Cl(PPh_3)(EPTH)]\cdot\frac{1}{3}CHCl_3$
2. $[Rh(CO)Cl(PPh_3)(EPH)]\cdot\frac{1}{3}CHCl_3$
3. $[Rh(CO)Cl(PPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$

Fig. VI.2.2   Electronic Spectra (in $CHCl_3$)

1. $[Rh(CO)Cl(AsPh_3)(EPH)]\cdot\frac{1}{3}CHCl_3$
2. $[Rh(CO)Cl(AsPh_3)(TPH)]\cdot\frac{1}{3}CHCl_3$
3. $[Rh(CO)Cl(AsPh_3)(ETH)]\cdot\frac{1}{3}CHCl_3$
4. $[Rh(CO)Cl(AsPh_3)(ETPH)]\cdot\frac{1}{3}CHCl_3$
5. $[Rh(CO)Cl(AsPh_3)(PPH)]\cdot\frac{1}{3}CHCl_3$

Fig. VI.3   Proton NMR Spectra (in $CDCl_3$)

1. $[Rh(CO)Cl(AsPh_3)(EPH)]\cdot\frac{1}{3}CHCl_3$

Fig. VI.1 IR Spectra
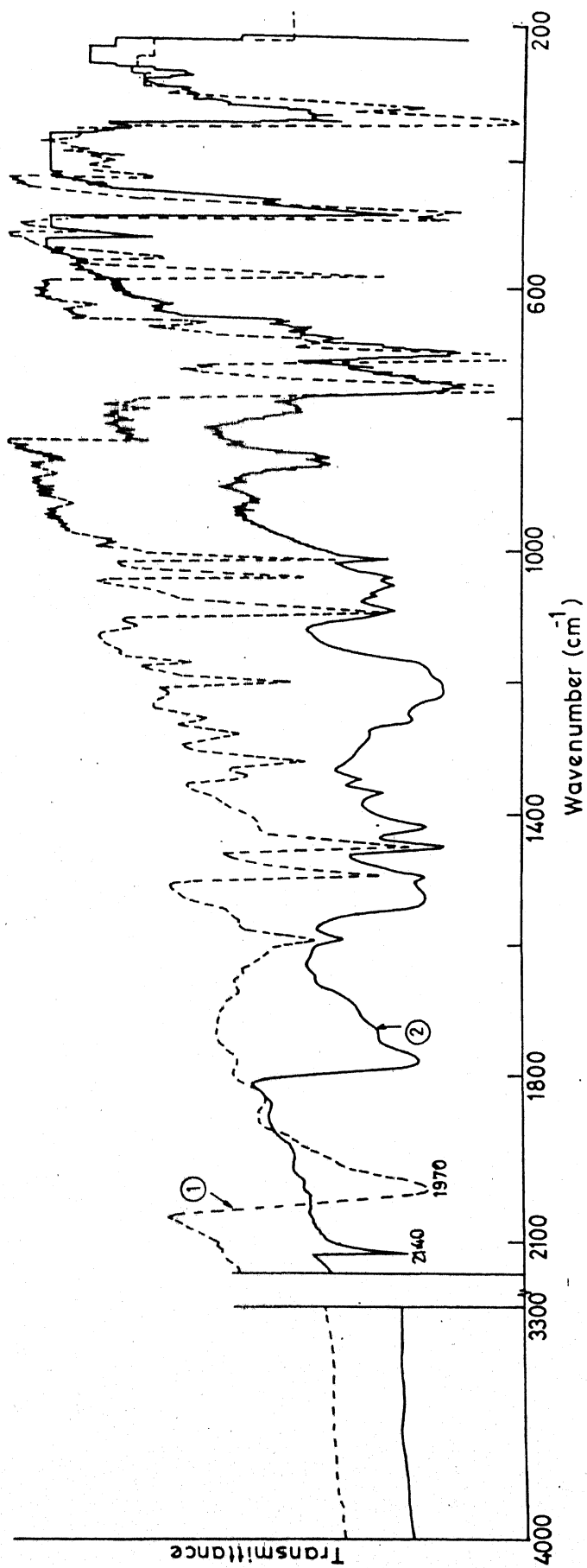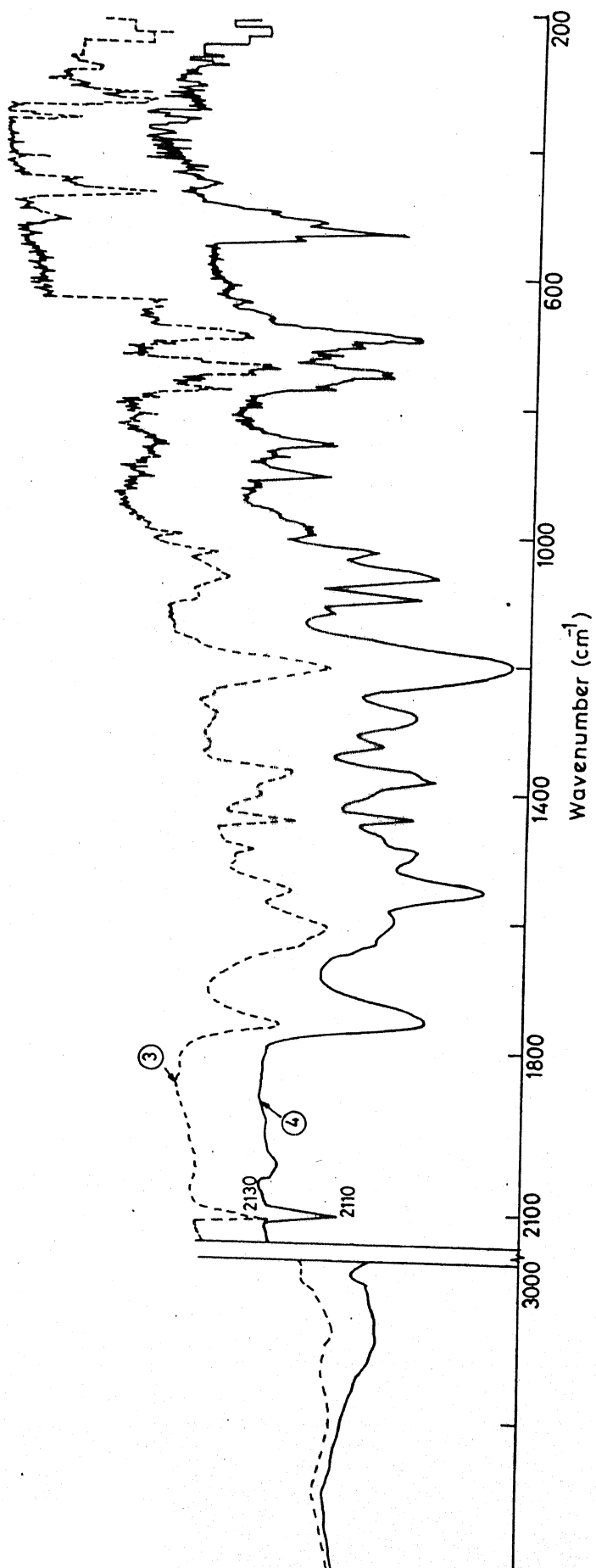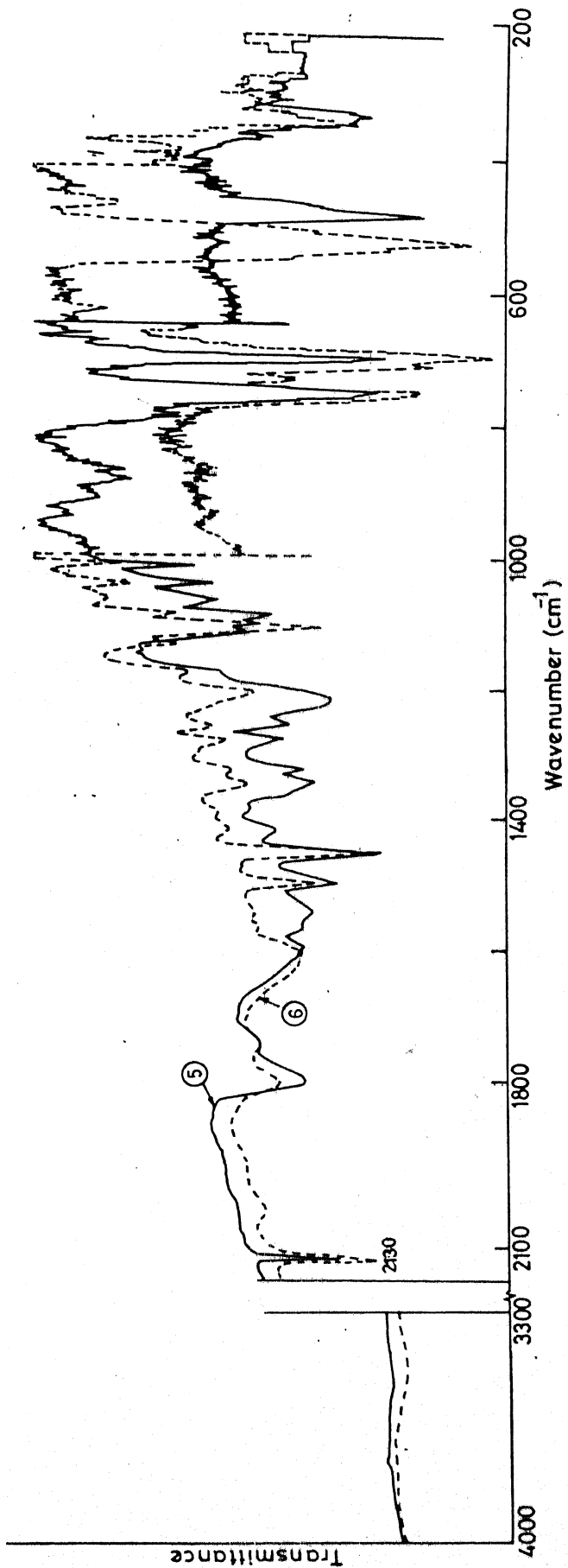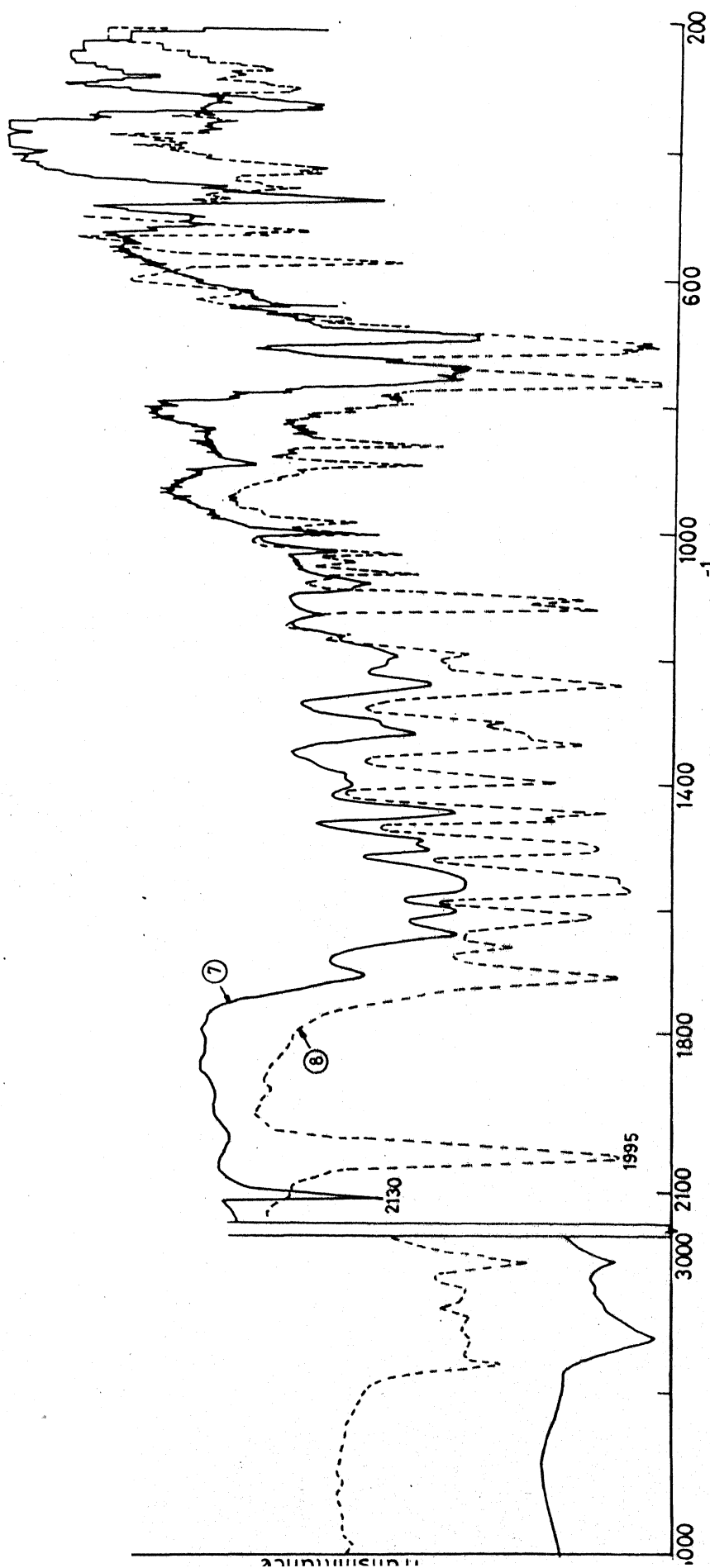
Fig. VI.1 IR Spectra

Fig.VI.1 IR Spectra

Fig.VI.1 IR Spectra

Fig. VI.1   IR Spectra
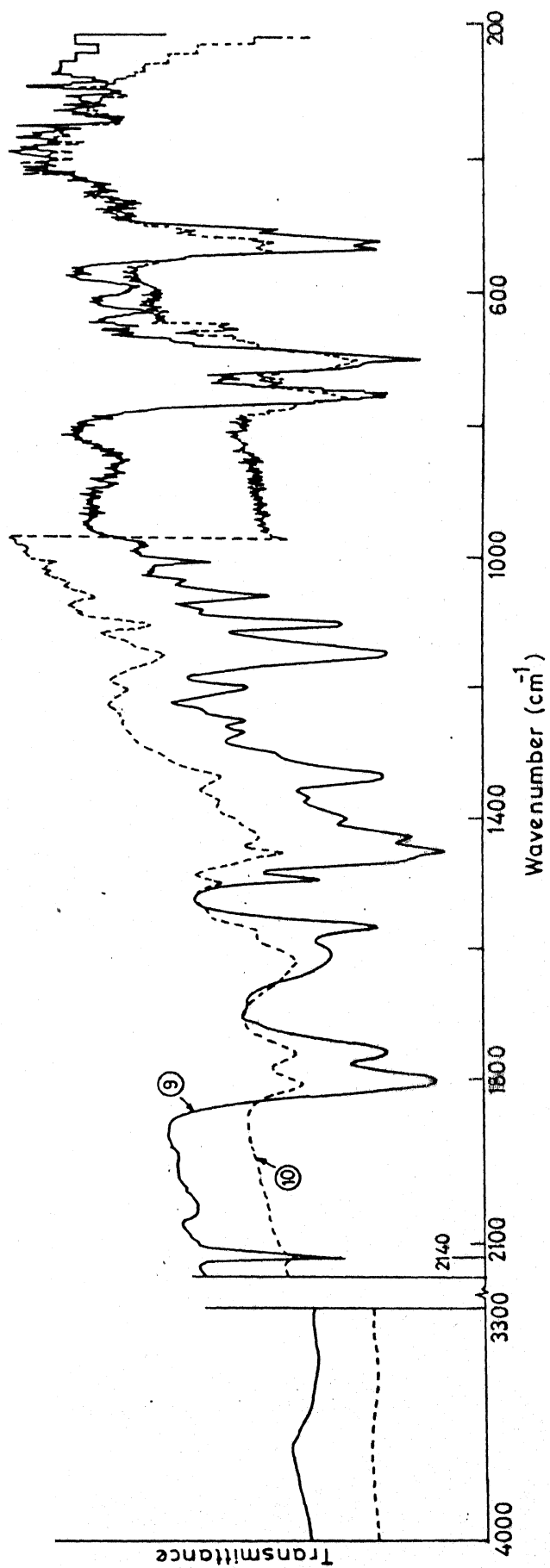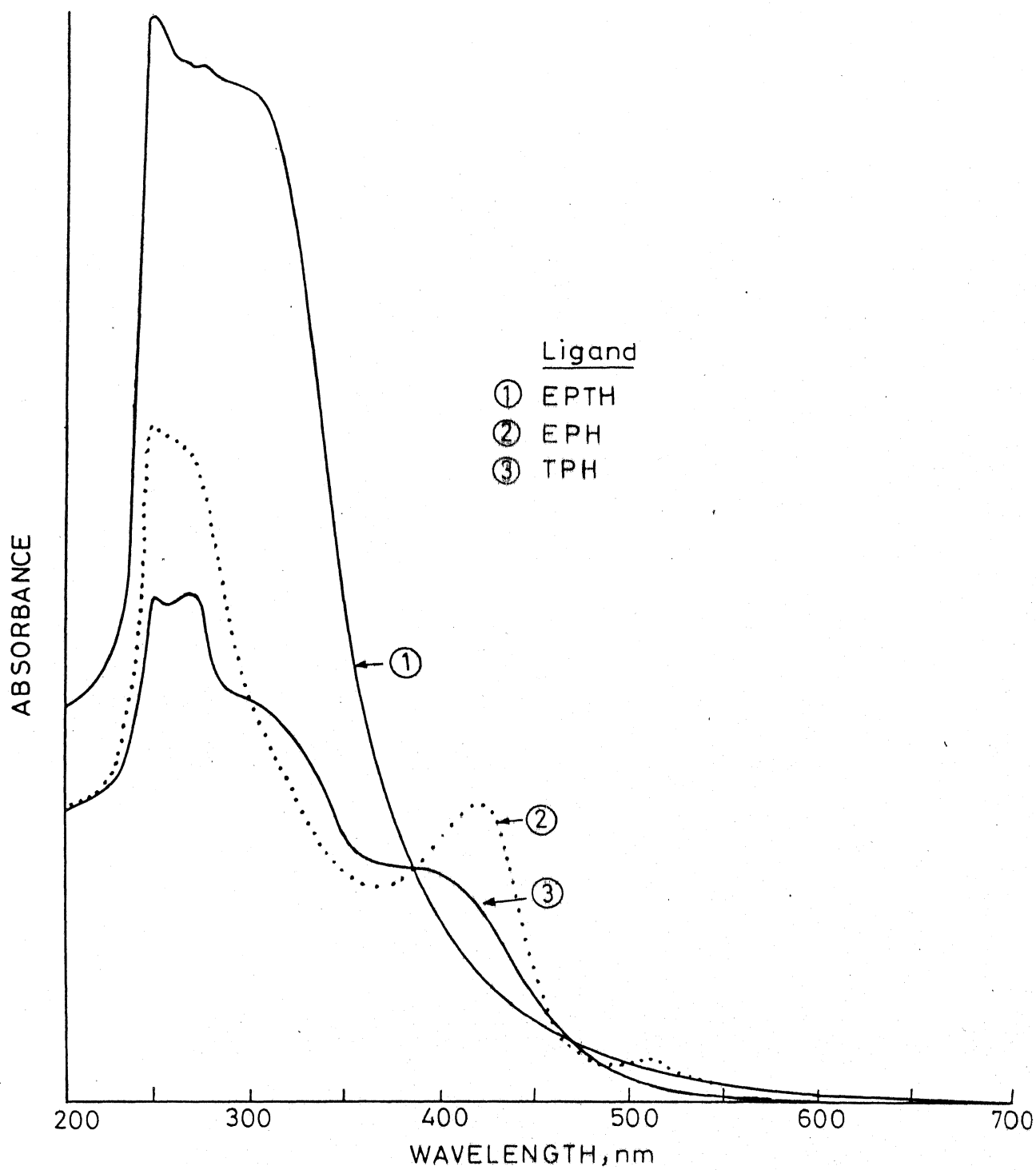
Fig. VI.2.1 Electronic spectra of [Rh (CO) Cl (PPh₃) (ligand)] 1/3 CH(

Ligand
① EPTH
② EPH
③ TPH
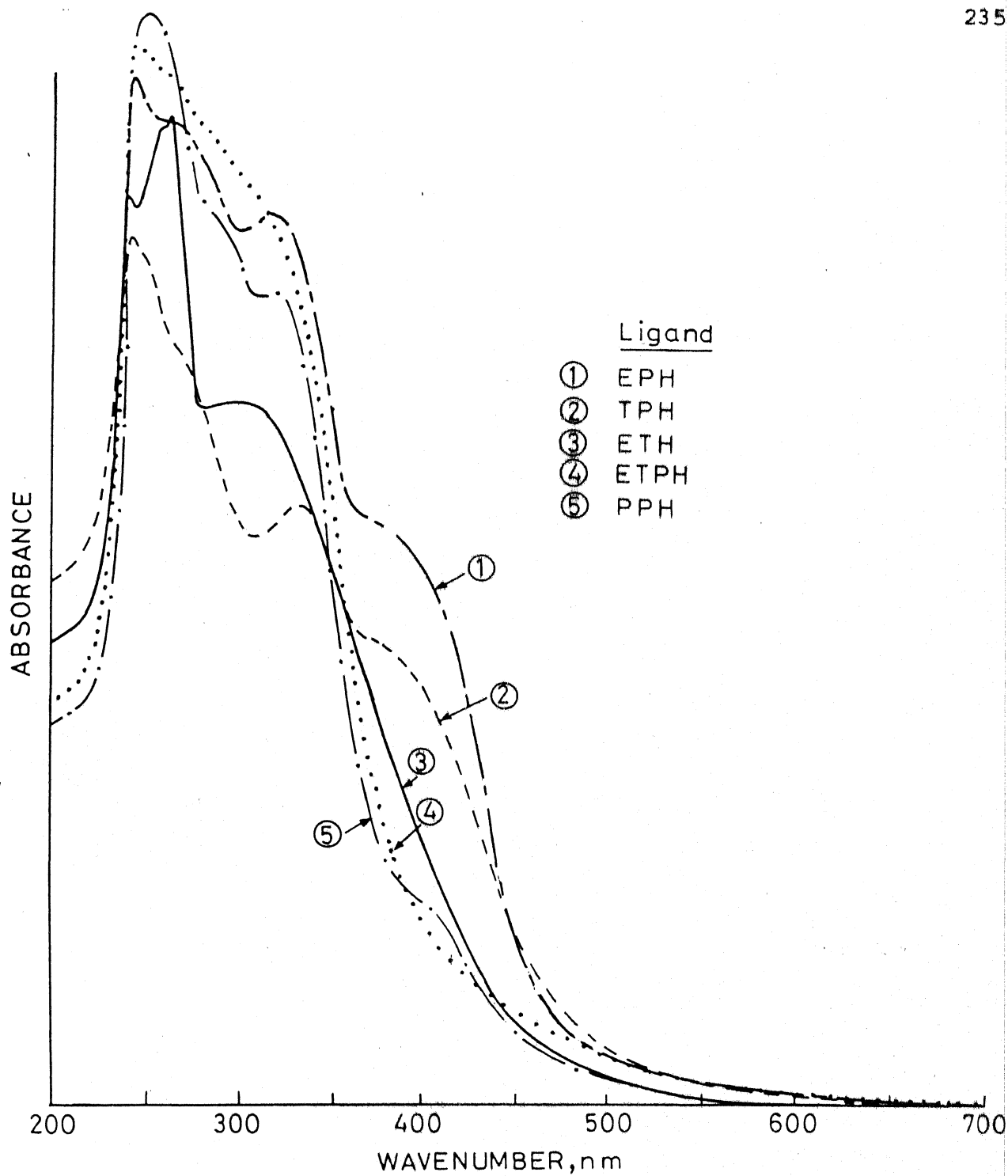
Fig. VI.22 Electronic spectra of [Rh (CO)Cl (AsPh$_3$)(ligand)] 1/3 CHCl$_3$

Ligand
① EPH
② TPH
③ ETH
④ ETPH
⑤ PPH

ABSORBANCE

WAVENUMBER, nm

Fig. VI.3 Proton NMR spectra

①

δ (ppm)

TMS
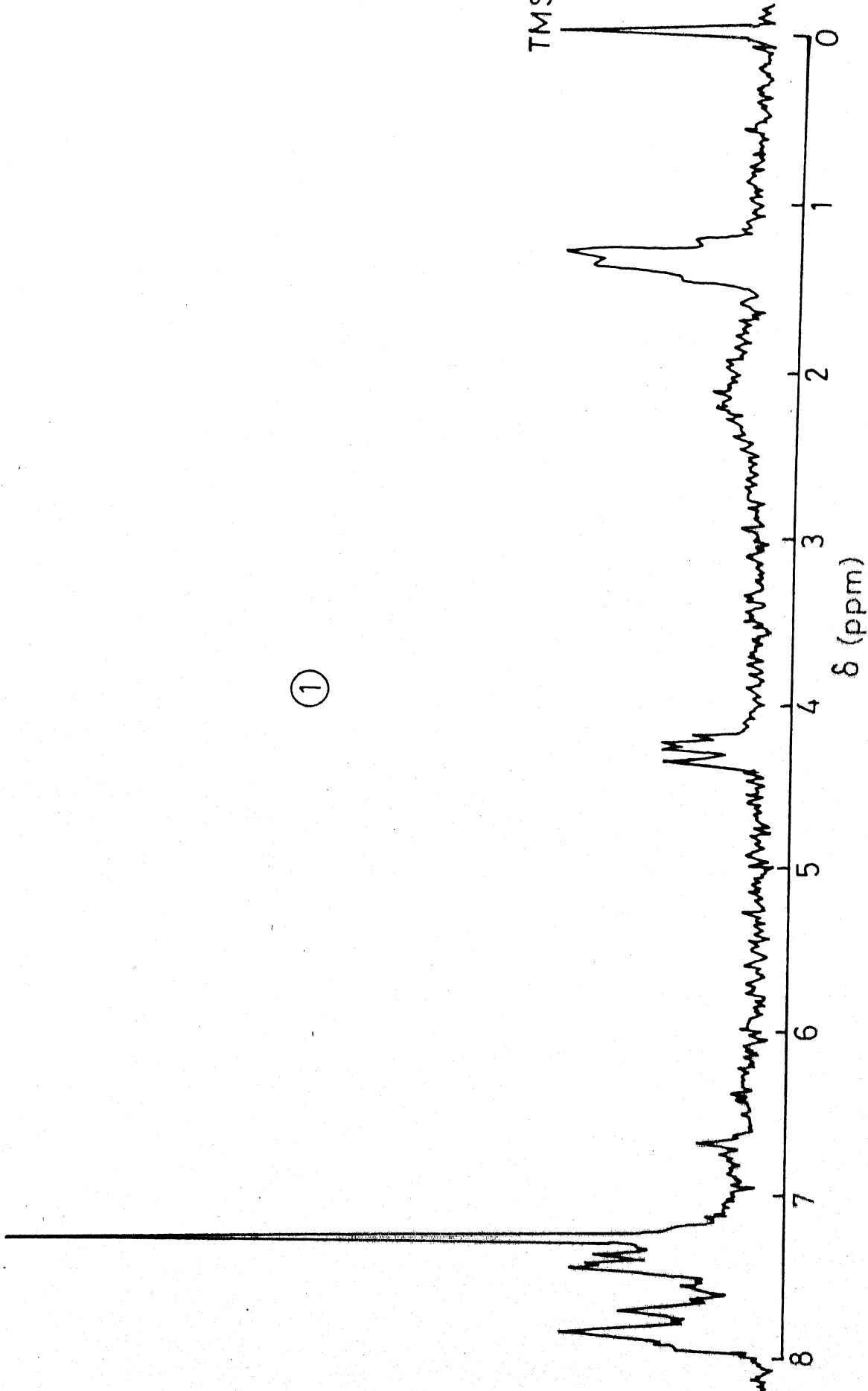
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